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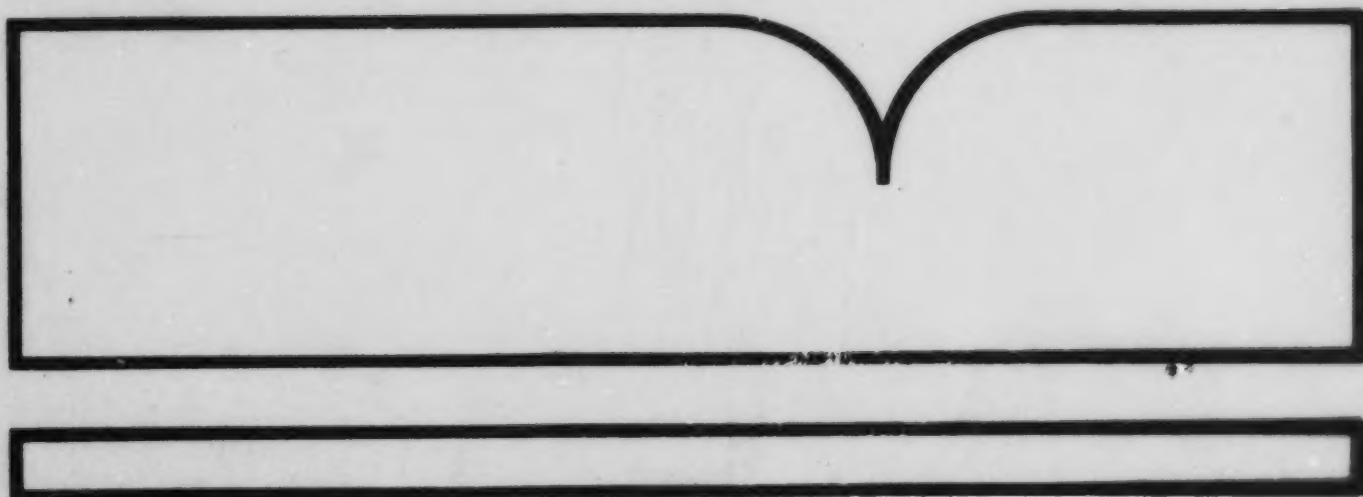
**Rates and Equilibria of Devolatilization and
Trace Element Evolution in Coal Pyrolysis**

North Carolina State Univ. at Raleigh

Prepared for

**Industrial Environmental Research Lab.
Research Triangle Park, NC**

Apr 82



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RATES AND EQUILIBRIA OF DEVOLATILIZATION AND
TRACE ELEMENT EVOLUTION IN COAL PYROLYSIS

by

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Office of Environmental Engineering and Technology
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16. ABSTRACT The report gives results of using a laminar-flow furnace to study the kinetics of devolatilization and evolution of S, As, Pb, and Hg in the pyrolysis of pulverized coal in nitrogen. Variables included pyrolysis time, reactor temperature, and coal type. Devolatilization rates and weight losses of the two subbituminous coals tested were lower than those of a bituminous coal. The four elements were released in significant quantities during rapid pyrolysis, with the elemental loss from the bituminous coal proceeding more rapidly and to a greater extent than that from the subbituminous coals. Emissions of As and Pb in subbituminous coal and Pb in bituminous coal were found to be proportional to the total volatile matter released. Emissions of Hg and As in bituminous coal were proportionately greater than the total volatile matter released. The S released was proportional to the amount of dry-ash-free volatile matter released for both coals. Five kinetic models for devolatilization were tested.			
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Coal Kinetics		Stationary Sources	
Pyrolysis Nitrogen		Devolatilization	
Vaporizing Sulfur		13B 14G	
Trace Elements Arsenic		08G, 21D 20K	
Chemical Analysis Lead (Metal)		07D 07B	
Mercury (Metal)		06A	
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ABSTRACT

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A laminar flow furnace has been used to study the kinetics of devolatilization and evolution of four elements--sulfur, arsenic, lead and mercury--in the pyrolysis of pulverized coal in nitrogen. The quantities varied in this study included pyrolysis time (170 msec-2 sec), reactor temperature (400-900 C), and parent coals (two low-swelling subbituminous coals and one medium-swelling bituminous coal). Weight losses were estimated using ash as a tracer. A Fisher Sulfur Analyzer was used to analyze the sulfur content of the feed coal and spent char, and atomic absorption spectrophotometry was used to analyze for the remaining three elements.

A previous report (Agreda, Felder, and Ferrell, 1979) described the experimental apparatus and analytical procedures, and presented preliminary data. Since then, the system has been modified and used to provide a data base for modeling the kinetics of rapid pyrolysis and pyrolysis equilibria for both high and low heating rates.

Weight losses of the coals studied increased significantly with time and temperature and approached different asymptotic values at different temperatures. The devolatilization rates and asymptotic weight losses of the subbituminous coals were lower than those of the bituminous coal. The elements were released in significant quantities during fast pyrolysis as temperature and time increased, with the elemental release from the bituminous coal proceeding more rapidly and to a greater extent than that from the lower rank coals. The emissions of arsenic and lead in subbituminous coal and lead in bituminous coal were found to be proportional to the total volatile matter release and the emissions of mercury and arsenic in bituminous coal were found to be proportionally greater than the total volatile matter release. The amount of sulfur released was found to be proportional to the amount of dry-ash-free volatile matter released for both coals.

Five kinetic models for devolatilization were tested. Among these, a two-parallel-reaction model due to Kobayashi provided the best correlation of the experimental data for the subbituminous coal and a distributed activation energy model due to Anthony was found best for the bituminous coal. A single first-order reaction model for elemental release coupled with a model for equilibrium release derived from batch pyrolysis experiments was used to correlate elemental release data.

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SECTION 1

INTRODUCTION

BACKGROUND

Coal represents approximately 70% of the recoverable fossil fuel resources in the United States and may eventually become our principal source of hydrocarbon fuel and chemical feedstocks. National recognition of the enormous immediate and long-range potential of coal has resulted in substantial efforts directed toward the development of an economically and environmentally viable coal utilization technology.

Coal conversion to clean gaseous and liquid products is especially attractive for alleviating the growing restrictions on existing consumption patterns. The main approaches to the conversion of coal to gaseous fuels are steam-oxidant gasification, hydrocarbonization, and pyrolysis (devolatilization). In all three processes, pyrolysis plays an important role. When coal is heated in any atmosphere, it releases volatile products. In most coal conversion processes coal is pulverized and subjected to rapid heating which causes a significant rate of devolatilization. The amount of volatile matter produced depends mainly on the type of coal, the temperature of the surrounding gas, the heating rate, the reacting pressure, and the size of the coal particles.

The effluent gases from a coal conversion system are known to contain elements in minor or trace amounts which are toxic to humans, animals, and plants, or cause severe corrosion in coal-fired boilers and gas turbines. These elements may exist as vapor and/or in association with particles in the effluent gases.

Studies have been made on the occurrence and distribution of trace elements in different coals (Gluskoter et al., 1977) and in effluents from coal-fired steam plants (Lyon, 1977) and coal gasification plants (Forney et al., 1975; Gasior et al., 1978). The data obtained in these studies provide a good qualitative picture of the pathways of trace and minor element constituents in coal gasification; however, they do not provide the detailed information about reactor conditions needed to predict the thermodynamics and kinetics of the release of these elements.

To be able to estimate the types and quantities of hazardous emissions released in the pyrolysis stage of steam/oxygen gasification or hydrogasification, it is necessary to measure and model the rates and

equilibria of both devolatilization and evolution of specific species. In Part I of this report (Agreda et al. 1979), an experimental system for performing these tasks was described. A batch furnace reactor was used to determine devolatilization and trace element release equilibria for slow pyrolysis at temperatures up to 1000°C, and a laminar flow reactor was used to measure emission rates for rapid pyrolysis. Preliminary results were obtained and used as the basis of modeling studies.

Subsequent to the publication of that report, the laminar flow reactor was modified in several ways, resulting in considerably higher precision and reproducibility in the data. Several existing devolatilization models were fit to the data by nonlinear regression, and the results were used to evaluate and compare the models. In addition, trace element evolution data were fit with a first-order rate law, and the results were used to draw inferences regarding the volatilities of these elements.

This document summarizes these experiments and results. The Fortran routines used for the experimental analysis and modeling are given by Kau (1980).

LITERATURE REVIEW

Coal Chemistry

Devolatilization of coal is a complicated process involving numerous chemical reactions coupled with the physical escape of volatile matter through the micropores of the coal. One of the difficulties in studying coal is that its chemical structure is not well defined, which tends to obscure the true mechanism of any occurring physico-chemical phenomenon.

Various physical and chemical methods have been used to elucidate the structure of coal, but completely satisfactory results have not yet been obtained. The general consensus (Tingey and Morrey, 1973) is that (1) coal consists of aromatic-aliphatic lamellae with three to five condensed rings per lamella, (2) sulfur and nitrogen are incorporated into hetero-cyclic rings, and (3) oxygen exists mainly as hydroxyl and carbonyl groups.

About 70-85 percent of total carbon in the bituminous coal is reported to be aromatic, 10-25 percent is hydroaromatic, and 4-5 percent is aliphatic. Aromatic carbon increases with an increase in the rank of the coal, but the sum of the aromatic and hydroaromatic fractions is almost constant (Mazumdar et al., 1966).

The organic material in coal is a heterogeneous mixture of organic minerals known as macerals. Macerals consist primarily of carbon, hydrogen, oxygen, and sulfur, and can be divided into three principal groups: vitrinite, exinite, and inertinite. Exinite has the highest hydrogen content, volatile matter content, and heating value, while inertinite has the least of all three. Inertinite has the highest degree of aromaticity, while exinite is the lowest in aromaticity. The properties of vitrinite are between those of the other groups.

Inorganic materials (ash) present in coal comprise from 5 to 20 percent of the total mass. The ash material includes quartz, pyrite, kaolite, illite, and calcite. The ash matter is distributed more or less uniformly and exists as small inclusions of variable composition and size. The ash inclusions range between 60 μm and 0.1 mm in average diameter.

Coal also contains many trace and minor elements. Out of 92 known non-transuranic elements, only 14 have not yet been found in coal (Loran and O'Hara, 1977). Sulfur occurs in coal in three forms: in organic combination as part of the coal substance, as pyrites or marcansite, and as sulfates. The amount of sulfur is normally not over 3%, but in exceptional cases it may be as much as 11%. The sulfates, mainly of calcium and iron, rarely exceed a few hundredths of a percent.

The major form of arsenic in coal is arsenopyrite (Duck and Himus, 1951). Most of the selenium in coal is thought to occur as selenopyrite (FeSeS). Anderson et al. (1979) reported that lead exists in coal as PbS ; however, it has also been reported that lead is associated almost entirely

with the organic fraction of coals. The forms of mercury in coal are not well established at this time.

The caking tendency of coal under rapid heating is assessed by the free-swelling index (FSI). A coal is non-caking if its FSI is below 1.0; weakly caking if its FSI is between 1.0 and 2.0; medium caking if its FSI is between 2.0 and 4.0; and strongly caking if its FSI is greater than 4.0.

The "Organic Affinity Index" is used to indicate whether certain elements are organic or inorganic constituents of the coal (Gluskoter et al., 1977). Ge, B, and Br are the elements with the highest organic affinities; Ni, Cu, Cr, and Hg tend to be present in both organic and inorganic combination; and Zn, Cd, Pb, and Fe are primarily associated with the inorganic matter (Kuhn et al., 1977).

Coal Devolatilization

When coal is heated to sufficiently high temperatures in an inert medium, it decomposes into two main components--volatile matter and solid residue. Volatile matter is a mixture of compounds of low molecular weight (e.g., hydrogen, oxides of carbon, methane) and high molecular weight (e.g., tar). The solid residue is a mixture of fixed carbon and ash.

There are five principal stages of devolatilization (Suuberg et al., 1978). The first stage involves moisture release around 100°C. Carbon dioxide and tar are evolved in the second stage between 350°C and 450°C. Chemically-formed water is released in the third stage between 500°C and 700°C. Carbon oxides, hydrocarbons, tar and hydrogen are released in the fourth stage, from 700°C to 900°C. In the last stage, at even higher temperatures, only carbon monoxide is formed.

The physical nature of coal devolatilization depends to a great extent on whether the coal is plastic or non-plastic. Plastic coals are also referred to as caking coals or strongly-swelling coals, since in the plastic state they are viscous liquid masses capable of coalescence and, upon resolidification, formation of a cake. The thermoplasticity of caking coals is manifested by softening, deformation, and resolidification upon heating. Plastic coals often devolatilize with the formation and eruption of bubbles, leaving a highly porous char containing entrapped bubbles. In extreme cases, the particles may swell to many times their original size, forming hollow char particles called cenospheres.

The temperature limits on the region of plasticity depend on the heating rate. At low heating rates, the plastic region is typically 420°C to 500°C with some variation among different coals, and at high heating rates, the plastic region extends to 2000°C or higher. The growth and escape of gas-filled bubbles constitutes an important mode of volatile transport in plastic coals.

Experimental Pyrolysis Studies

There have been many coal pyrolysis experiments carried out under rapid heating conditions by different researchers. These include entrained flow reactor experiments (Agreda, 1979; Nsakala, 1976; Kobayashi, 1976; Coates et al., 1974; Stickler et al., 1974; Badzioch and Hawksley, 1970; Kimber and Gray, 1967; Eddinger et al., 1966) and electrical screen heating (Suuberg et al., 1978; Menster, 1974; and Anthony et al., 1975).

Loison and Chauvin (1964) studied the products of coal pyrolyzed under a fairly high rate of heating. The experimental method consisted of packing 50-80 μm coal particles in a thin layer into a 50 μm metal gauze, and then heating the gauze electrically at a rate of about $1500^{\circ}\text{C}/\text{sec}$ to a final pyrolysis temperature of about 1050°C . Secondary cracking reactions were avoided by ejecting the products into a cold atmosphere of nitrogen. The results showed that the volatile matter yield was sometimes greater than that obtained by the traditional method (slow heating rate), and always greater than the change in proximate volatile matter between the original coal and resulting char. Rapid pyrolysis gave a high tar/gas ratio, the highest yield of tar being 27% of dry ash-free coal, as opposed to 16% for slow pyrolysis.

Badzioch and Hawksley (1970) carried out extensive experiments on the pyrolysis of ten British coals of various ranks in a laminar flow reactor. Pyrolysis in a nitrogen atmosphere was studied as a function of isothermal reaction time (20-100 milliseconds), temperature (400°C - 1000°C), and heating rate (25,000-50,000 $^{\circ}\text{C}/\text{sec}$). Several results emerged in these studies: (1) the weight loss was always greater than the change in proximate volatile matter between the original coal and resulting char, by a factor (referred to as the Q-factor) of 1.35-1.8, depending on which coal was studied; (2) the weight loss (i.e., volatile matter yield) increased with final temperature, duration of pyrolysis, and to a smaller extent, heating rate; and (3) pyrolysis was independent of particle size between 20 to 60 μm . These results are in good agreement with those of Kimber and Gray (1967), who used a laminar flow reactor similar to Badzioch and Hawksley's, but pyrolyzed their samples at much higher temperatures.

Gray et al. (1974) determined weight loss as a function of bed height in a crucible, finding that the deeper the bed, the lower the weight loss. Varying the initial weight of sample in the crucible from about 0.25 to about 3.5 grams brought about a decrease in weight loss of about 4 percent. Their Q-factor of 1.1 fell below those found by Badzioch and Hawksley (1.35 to 1.8).

Gray et al. (1974) observed higher volatile loss with higher heating rate. When coal is taken to its final temperature very rapidly, the material pyrolyzing is essentially raw and unordered and is thus susceptible to more extensive pyrolysis than a more ordered structure. Conversely, when coal is heated slowly, the material reaches the final temperature partially pyrolyzed but more ordered than the raw coal and thus is susceptible to less extensive pyrolysis. Moreover, in proximate volatile matter determinations, the upper

part of the samples can easily act as a trap for volatiles undergoing secondary cracking.

Anthony et al. (1976) used a system similar to Loison and Chauvin's to study the pyrolysis of a Pittsburgh seam bituminous coal and a Montana lignite. Pyrolysis rates, measured by weighing the samples before and after electrical pulse heating for intervals of known duration, were determined as a function of total residence time (0.05-20 seconds), heating rate (10^2 - 10^4 °C/sec), particle size (50-100 μ m), pressure (.001-200 atm), and temperature 400-1000°C).

Weight loss was found by Anthony to be independent of particle size, pressure, and heating rate for the lignite; that is, it varied only with temperature and time. For the bituminous coal, weight loss increased with decreasing pressure, decreasing particle size, and to a small extent with increasing heating rate. The kinetics of primary decomposition were described by a set of independent first-order parallel reactions with an activation energy distributed normally around a mean of 49 ± 10 kcal/mole for the bituminous coal. The authors proposed that conditions which affect the occurrence of secondary reactions (e.g., pressure, particle size) were more important in determining volatiles yield than was the heating rate.

In work reported in the predecessor of the present study, Agreda et al. (1979) measured the extent of thermal decomposition of size-graded particles of three coals using a laminar flow vertical furnace. Coal particles were injected with cold carrier gas into a preheated nitrogen stream in a cylindrical alumina tube. The ambient gas temperature ranged from 400°C to 900°C and particle residence times ranged from 0.2s to 1.2s. Weight loss was determined by using ash as a tracer. Agreda's results show that coal appears to approach a quasi-equilibrium volatile yield in fast pyrolysis, which is below the equilibrium volatile yield in slow pyrolysis. Agreda's quasi-equilibrium results showed good agreement with those of Suuberg et al. (1978), although two different types of apparatus were used in these two studies.

The effect of the heating rate on volatiles yield and product distribution is a strong function of the coal type. At higher heating rates (1000-7000°C/s) the volatile yield and tar to gas ratio of the product are larger than those obtained at low to moderate heating rates (1-200°C/s), and this effect decreases with decreasing coal rank (Badzioch and Hawksley, 1970). Almost no heating rate effects were observed by Kobayashi (1976) for lignite coals if the heating rate exceeded a critical value. Similarly, Anthony (1974) reported no effects on volatile yield when the heating rate was increased from 600 to 10000°C/s for a final temperature of 1000°C.

Pressure effects on the volatile yield are dependent on coal rank. No pressure effect was observed for lignite coal, and lower pressure was found to favor the release of volatile matter for bituminous coal (Anthony et al., 1976). Anthony et al. (1976) and Nsakala (1976) found a strong particle size effect on the volatile yield, but contradictory results were obtained by Badzioch and Hawksley (1970).

Pyrolysis Models

The simplest pyrolysis model takes the rate of volatile yield to be proportional to the remaining volatile matter.

$$dV/dt = K (V_f - V) \quad (1.1)$$

$$K = B e^{-E/RT} \quad (1.2)$$

where

V = volatiles lost up to time t , expressed as a fraction of the original coal weight;

V_f = volatiles lost after infinite time (ultimate yield), expressed as a fraction or percentage of the original coal weight;

t = time;

T = temperature;

E = activation energy;

B = frequency factor.

Many investigators have focused on determining the unknown parameters B and E . Variations of several orders of magnitude are observed. Some may be attributed to the differences in the structure of coal and physical factors, such as particle size; however, their extent appears to be too large to be explained solely by these factors. It appears evident that the first-order rate law parameters obtained by different investigators are strongly dependent on the experimental apparatus employed. The devolatilization rates obtained by different investigators are shown in Table 1.1.

Badzioch and Hawksley (1970) proposed the following empirical model:

$$V^* = Q W_p (1 - c) \{1 - \exp [-at_I \exp (-b/T)]\} \quad (1.3)$$

$$c = \exp [-k_1 (T - k_2)] \quad (1.3a)$$

where

V^* = weight loss on a dry ash-free basis

W_p = proximate volatile matter of coal;

t_I = isothermal reaction time; and

Q, a, b, k_1, k_2 = empirically determined constants.

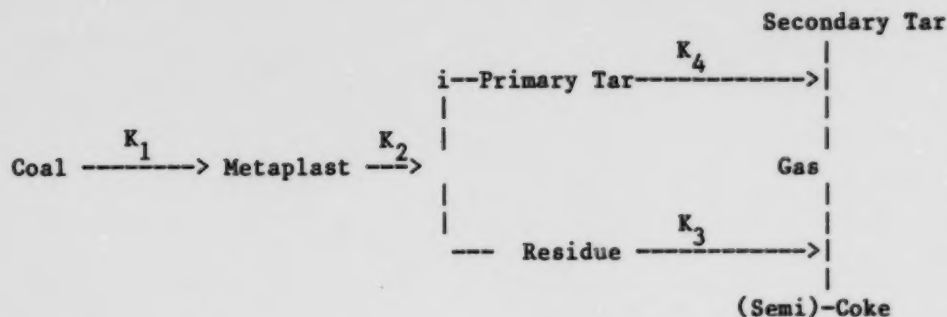
Badzioch and Hawksley found that c was equal to 0.14 for all nonswelling coals.

The above model is based on the consideration of devolatilization as a single first-order overall reaction, and was successfully used by Nsakala (1976) to correlate data from laminar flow furnaces. Excellent fit of high dry- ash-free weight loss data between 750°C and 1000°C was obtained. However, Horton (1979) indicates that this model lacks the flexibility required to describe much of the experimental data available and may be inadequate to describe nonisothermal pyrolysis.

More complicated models involving more than one reaction have been developed to describe different aspects of devolatilization phenomena. van Krevelen and his coworkers (Fitzgerald and van Krevelen, 1959; Chermin and van Krevelen, 1957; Van Krevelen et al., 1956) developed a multiple consecutive reaction pyrolysis model:

Table 1.1 Coal properties and devolatilization rate parameters

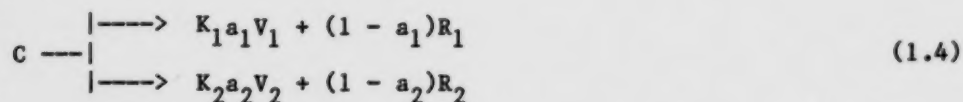
Investigators	Coal	E (kcal/mole)	B	Apparatus
Badzioch and Hawksley (1970)	BNCB 902	17.8	1.14×10^5	Laminar
	FNCB 601	17.8	3.12×10^5	
Anthony et al. (1975)	Pittsburgh seam bituminous	13.3	1.80×10^3	Wired Screen heating
	Montana lignite	20.0	2.9×10^5	
Kobayashi (1976)	Pittsburgh seam bituminous	25.0	6.6×10^4	Laminar
	Montana lignite	25.0	6.6×10^4	Laminar



"Metaplast" is an intermediate product responsible for the fluidity of coal. Quantitative evaluation of the rate constants K_1 , K_2 , and K_3 was performed for some coals (assuming first-order reactions)¹ yielding good agreement with the experimental results. However, this model was developed only for slow heating conditions and may not be valid for modeling the evolution of volatile matter in fast pyrolysis (Kimber and Gray, 1967; Eddinger et al., 1966).

Multiple parallel reaction models have been used by several investigators. Chukhanov (1954) postulated a model involving five first-order reactions with different activation energies and frequency factors. Reidelbach and Summerfield (1975) proposed a set of ten parallel reactions to describe the process of pyrolysis. The model was later refined by Reidelbach and Algermissen (1976).

Kobayashi (1972) proposed and later successfully used a model which consists of the following pair of parallel, first order, irreversible reactions.



$$K_1 = B_1 e^{-E_1/RT} \quad (1.4a)$$

$$K_2 = B_2 e^{-E_2/RT} \quad (1.4b)$$

where

a_1, a_2 = mass stoichiometric coefficients;

V_1, V_2 = volatile yields;

R_1, R_2 = char yields;

K_1, K_2 = Arrhenius rate constants

and $E_1 < E_2$.

The rate equations are as follows:

$$\frac{dV_1^*}{dt} = -a_1 K_1 \frac{dW^*}{dt} \quad (1.5)$$

$$\frac{dV_2^*}{dt} = -a_2 K_2 \frac{dW^*}{dt} \quad (1.6)$$

$$V^* = V_2^* + V_1^* \quad (1.7)$$

where

W^* = dry-ash-free mass of coal

V^* = dry-ash-free weight loss

W_0 = original d.a.f. mass of coal

Integration of the above equations results in the following expression for the overall weight loss:

$$V^* = \frac{V_1^* + V_2^*}{W_0^*} = \int_0^{t_R} dt (a_1 K_1 + a_2 K_2) \exp\left[-\int_0^t (K_1 + K_2) dt'\right] \quad (1.8)$$

Under isothermal conditions, Equation 1.8 can be integrated to give:

$$V^* = \frac{a_1 K_1 + a_2 K_2}{K_1 + K_2} \{1 - \exp[-(K_1 + K_2)t_R]\} \quad (1.9)$$

The asymptotic value of V^* under isothermal conditions is given by:

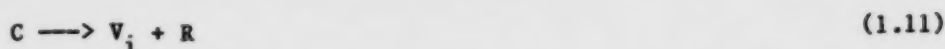
$$V_f^* = \frac{a_1 K_1 + a_2 K_2}{K_1 + K_2} \quad (1.10)$$

This equation shows that the asymptotic weight loss is a weighted average of

a_1 and a_2 , the asymptotic values of weight loss at low and high temperatures, respectively. Hence, a value of $a_2 = 1$ may be assigned as complete weight loss is expected at high temperatures. Kobayashi (1976) proposes a constant value of $a_1 = 0.3$.

Kobayashi (1976) integrated Equation 1.8 numerically and obtained excellent correlations of data for a bituminous coal and a lignite coal by applying the same set of parameters to both coals. However, as we shall find out later in this study, the parameters do not appear consistent when applied to other coals.

The most generally accepted model developed to date is that of Anthony (1974), who assumed that the thermal decomposition of a coal molecule consists of a large number of independent first-order decomposition reactions, each having a different activation energy but all having the same pre-exponential factor. The rate equations are:



$$\frac{dV_i}{dt} = K_i (V_{if} - V_i) \quad (1.12)$$

$$K_i = B_i \exp(-E_i/RT) \quad (1.13)$$

The subscript "i" is used to denote a particular reaction. Anthony (1974) proposed a Gaussian distribution of activation energies. According to this model, the volatiles yield is given by the relation:

$$(V_f^* - V^*)/V_f^* = \exp(-\int_0^t K dt) f(E) dE \quad (1.14)$$

$$f(E) = [(s(2\pi)^{1/2})^{1/2} \exp[-(E-E_0)^2/2s^2]] \quad (1.15)$$

$$K = B \exp(-E/RT) \quad (1.16)$$

where

E_0 = mean activation energy;

s = standard deviation of the activation energy distribution;

Anthony et al. (1975) used this model to correlate pyrolysis data for one lignite coal and one bituminous coal, integrating the activation energy distribution from $E_0 - 2s$ to $E_0 + 2s$ numerically. He obtained an excellent correlation. Anthony also showed that a distribution of activation energies from 30-70 kcal/mole leads to the apparent single step activation energy of 10-20 kcal/mole observed by a number of investigators and attributed to diffusion control of the rate. Suuberg et al. (1978) determined the

kinetics of the pyrolysis of several coals and used Anthony's (1976) model to fit his data. The distribution of activation energies obtained in this study was similar to that obtained by Anthony.

Agreda (1979) proposed a single-step model with rate equation

$$dV^*/dt = K(V_f^* - V^*) \quad (1.17)$$

$$K = B \exp(-E/RT) \quad (1.18)$$

As t approaches infinity, $V^* \rightarrow V_f^*$

At $t = 0$, $V^* = 0$.

The parameters K and V_f^* are functions of particle temperature, which in turn is a function of time. Equation 1.17 is a linear ordinary differential equation which may be solved by using an integrating factor, yielding

$$V^* = \frac{\int_0^{t_R} dt K(V_f^*) \exp(\int_0^t K dt)}{\exp(\int_0^{t_R} K dt)} \quad (1.19)$$

Values of V_f^* at each temperature can be obtained from asymptotic d.a.f. weight losses obtained in the laminar flow furnace experiments, or from equilibrium yields in the batch experiments (slow pyrolysis). Agreda used both methods and fit the data with a fourth-order polynomial,

$$V_f^* = B_0 + B_1(T/100) + B_2(T/100)^2 + B_3(T/100)^3 + B_4(T/100)^4 \quad (1.20)$$

This polynomial, which is valid for a temperature range of 400-900°C, was then used in Equation 1.19 to calculate overall d.a.f. weight losses.

Agreda et al. (1979) applied this model to three coals: Montana Rosebud (subbituminous), North Barber No. 8 (New Mexico subbituminous), and Beulah Zap (North Dakota lignite). He obtained good correlations applying the same set of parameters to all three coals. However, he used a trial-and-error method to obtain the parameters. Use of a more systematic regression technique could alter Agreda's conclusion that the parameters are independent of coal type. The application of such a technique is one of the objectives of the present study.

Elemental Release During Pyrolysis

Physical and chemical demineralization of coals have shown that most trace and minor elements are associated with mineral matter (Kuhn et al., 1977). Since minerals cannot be totally removed by current commercial cleaning procedures, their volatilities are important with respect to coal processing.

Kobayashi (1976) reported that the release of sulfur in chars during pyrolysis of coal increases as residence time and temperature increase, and may be as high as 80%. Kuhn et al. (1977) found that most of the evolved sulfur was lost while coal was heated between 300°C and 400°C. Only a small additional amount of sulfur was evolved when char was further heated to 700°C. Two-thirds of the sulfur initially in the coal was ultimately released.

Agreda (1979) studied the volatility of sulfur in both crucible and laminar flow experiments. Like Kuhn et al. (1977), Agreda found that the release of sulfur is very rapid at first, becoming slower as time progresses, and finally approaching an asymptotic limit. Seventy-five percent sulfur release was reported by Agreda. Suuberg et al. (1978) carried out experiments at temperatures ranging from 400°C to 1200°C and residence times ranging from 5 to 30 sec in an electrical screen furnace. They reported that sulfur release from coal during pyrolysis can be as high as 60% of the original mass present.

Several investigators have studied the evolution of trace elements in both slow and fast pyrolysis. Ting (1979) carried out experiments in a quartz furnace by inserting a coal-loaded crucible boat into a preheated helium atmosphere. The effluent gases, tars and solid residue were analyzed for arsenic and selenium: 62.8% volatility of Se and 49.3% volatility of As were found. Agreda (1979) reported that in batch experiments Sm, Cr, Th, Sc, Fe, and Co are retained completely, and As, Se, and perhaps La exhibit intermediate volatility (< 50% release). Mercury and chlorine show losses of greater than 70% at temperatures below 700°C, and more than 75% of lead is released at temperatures above 1000°C. These results apply to coals with ranks ranging from lignite to anthracite. Agreda (1979) also found that Fe, Co, Sc, Na, Ce, and V are completely retained in the chars produced in laminar flow reaction experiments, and C, H, S, As, Se, Pb, and Hg are released in significant quantities.

Shiley et al. (1978) reported that elements which exhibit significant devolatilization (>30%) from bituminous coals heated in steps to 450°C and 700°C in a batch reactor under a N₂ atmosphere include P, Cl, S, As, Br, I, Pb, Se, Te, and Zn. Another group that exhibits moderate to significant losses (<30%) in some coals includes Cd, Cu, La, Li, Rb, Sb, Sm, Sr, U, Yb, and possibly Al. Lignite is reported to exhibit significant devolatilization losses of Si, K, Ti, Dy, Ga, Hf, Ni, and Sc in addition to most of the elements listed for bituminous coals. Elements which appear to be retained in the majority of chars, except those from lignitic coals, include Si, Mg,

Ca, Fe, Na, Ti, Ba, Ce, Co, Cr, Cs, Dy, Eu, Ga, Hf, Lu, Mn, Ni, Sc, Ta, Tb, Th, and V. Shiley et al. (1978) reported inconclusive results, due to poor statistics caused by extremely low concentrations, for Ag, Au, In, Mo, and W.

The weight and elemental losses found by Kuhn et al. (1977) and Shiley et al. (1978) are shown in Table 1.2. Shiley et al. (1978) emphasize that only volatility ranges can be given because the overall statistical errors involved in sampling, pyrolysis, and analysis reflect significant uncertainties. Percent relative standard deviation (% RSD) values for elements range from 5% - 10% in the case of minor elements to 20% - 40% for some trace elements. The % RSD includes cumulative errors due to inhomogeneous samples, poor counting statistics, contamination, etc., for each coal or char.

Table 1.2. Weight loss during pyrolysis (from Kuhn et al., 1977)

Sample Number	Seam and State	Percentage Weight Loss	
		at 450°	at 700°
C 18857	No. 6 Illinois	32.2	34.3
C 18571	No. 6 Illinois	27.5	21.5
C 18571F	No. 6 Illinois	30.3	40.5
C 18440	Lignite North Dakota	33.9	44.1
C 18185	No. 5 Illinois	27.0	37.1
C 18847	Blue Creek Alaska	8.4	17.0

Trace Element Chemistry

Duck and Himus (1951) suggest that the major form of arsenic in coal is arsenopyrite. When the temperature exceeds 820°K, arsenopyrite begins to decompose into pyrrhotite (FeS) and metallic arsenic:



The major form of selenium in coal is thought to be selenopyrite (FeSeS). It decomposes into pyrrhotite (FeS) and elemental Se upon heating:



Solomon (1977) reported that as much as 60% of organic sulfur in coal resides in thiophene rings. Attari et al. (1976) observed that sulfur side chains (-SH) and linking sulfur chains (-S-) rupture first in the heating sequence during pulverized coal pyrolysis, leading to sulfur evolution at low temperature. The thiophene structure, however, is more stable and does not decompose until temperatures of about 1000° C are attained.

Anderson et al. (1979) reported that lead exists in coal as PbS. However, it has also been reported that lead is associated almost entirely with the organic fraction of coals. The chemical forms of mercury in coal are not known; however, evidence suggests that metallic mercury is released during pyrolysis.

Agreda (1979) tried to model the release of trace elements using a first-order rate equation:

$$dZ^*/dt = K (Z_f^* - Z^*) \quad (1.21)$$

where

Z^* = d.a.f evolution of element in question

Z_f^* = asymptotic (large time) value of Z^*

$$K = B \exp(-E/RT) \quad (1.22)$$

Equation 1.21 is a linear ordinary differential equation which is solved using an integrating factor, yielding

$$Z^* = \frac{\int_0^{t_R} dt K Z_f^* \exp\left[\int_0^t K dt'\right]}{\exp\left[\int_0^{t_R} K dt\right]} \quad (1.23)$$

Values of DZ_f^* at each temperature can be obtained from the relation (Agreda, 1979):

$$Z_f^* = H [T - T_C] Z_{fe}^* [1 - e^{-b(T - T_C)}] \quad (1.24)$$

where

$H[T - T_C]$ = unit step function

T_C = critical temperature at which elemental release begins

Z_{fe}^* = high temperature limit of Z_f^*

b = constant

Values of b , T_C , and Z_{fe}^* for S, Hg, Pb, and As determined by Agreda (1979) are shown in Table 1.3. Unfortunately, Agreda (1979) could not obtain good correlations with his fast pyrolysis data due to uncertainties in analysis and statistical errors associated with sampling.

In the absence of good kinetic parameters for the elemental release model, a simple linear correlation model was proposed as a rule of thumb to predict rates of elemental release (Agreda, 1979):

$$Z^* = K_s V^* H[T - T_C], \quad V^* < V_f^*(T) \quad (1.25)$$

This model presumes that an element is not released until T reaches T_C , and thereafter release occurs at a rate proportional to the rate of d.a.f. weight loss. Agreda (1979) found that sulfur has the highest correlation with the d.a.f. weight loss of all elements studied, with K_s equal to 1.0. The reason for the extent of this correlation is not clear since sulfur exists in at least three primary forms in coal (pyrites, sulfates, and organically bound sulfur). A possible explanation could be inferred from the findings of Kuhn et al. (1977), who reported that the pyrite contained in coal is converted to pyrrhotite and sulfur at 450°C or lower in a nitrogen atmosphere. Chemical analyses also indicate a greater loss of sulfur from the pyrites than from organic sulfur at low temperature, whereas the reverse was found to be true at high temperatures (450°C). Furthermore, pyrites react with carbon to form carbonyl sulfide and decompose, releasing sulfur in gaseous form (Agreda, 1979).

Table 1.3 Equilibrium elemental release model parameters
(from Agreda, 1979)

Element	$T_C(^{\circ}\text{C})$	$Z_f^*(\%)$	$b(1/^{\circ}\text{C})$
As	223	66.3	8.8×10^{-4}
Se	223	55.4	48.2×10^{-4}
Pb	449	100.0	26.6×10^{-4}
S	223	77.1	20.1×10^{-4}
Cl	234	100.0	39.4×10^{-4}
Hg	110	97.3	25.8×10^{-4}

SECTION 2

EXPERIMENT

PREPARATION OF COAL SAMPLES

Experiments were performed on two coals in this study: North Barber No. 8 seam HVC subbituminous coal, Navajo Mine New Mexico (NB8) and Western Kentucky No. 11 HVB bituminous coal (WK11). A summary of data on these coals is presented in Table 2.1.

Table 2.1 Coal characterization data

Coal Characterization					Proximate Analysis		
Coal	Code	Rank	FSI	Moisture	Ash	Volatile	Fixed
NM							
No. 8	NB8	HVC	0.5	10.09	18.32	33.80	37.79
W. K.							
No. 11	WK11	NVB	2.5	6.34	15.02	34.67	43.97
Ultimate Analysis(%)					Sulfur Forms(%)		
	C	N	H	S	Pyritic	Sulfatic	Organic
NM							
No. 8	55.18	1.21	4.12	0.73	0.31	0.0	0.42
W. K.							
No. 11	60.07	1.775	4.28	4.64	2.63	0.14	1.87

Coal samples were crushed in a Bico pulverizer with ceramic plates and in a small porcelain ball mill. The pulverized coal was then size-graded with U. S. standard sieves and a mechanical shaker, and the 325-400 mesh size fractions of NB8 and WK11 coals were retained for use in the experiments. The following average particle properties, also used by Kobayashi (1976) and Agreda et al. (1979), were used:

heat capacity: $C_p = 0.25 \text{ cal/g K}$

density: $d_p = 1.25 \text{ g/cm}^3$

emissivity: $e_p = 0.9$

thermal conductivity: $k = 3.0 \times 10^{-3} \text{ cal/cm sec K}$

mean particle diameter: $D = 41.5 \text{ um}$

EXPERIMENTAL EQUIPMENT

The experimental equipment used by Agreda et al. (1979) was also used in this study. Changes (to be discussed later in this section) were made to modify the collector cooling system. This equipment resembles that used by Badzioch and Hawksley (1970). It was specifically designed to accomplish the following functions:

1. Feed coal particles into a reaction zone of known length (residence time);
2. Raise the temperature of the coal particles as rapidly as possible (i.e., at a rate greater than $10^4 \text{ }^\circ\text{C/sec}$) to the predetermined pyrolysis temperature;
3. Quench all the pyrolysis reactions as rapidly as possible following collection to prevent conversion through secondary reactions;
4. Separate solid (i.e., char) from gaseous (i.e., volatile matter plus carrier gas) products and prevent volatile matter from depositing on the surface of the solid.

Laminar Flow Reactor System

A schematic of the laminar flow furnace system, feeder subsystem, char collection apparatus, and exhaust and suction subsystem is shown in Figure 2.1. The furnace is made of alumina with an inside diameter of 8 cm and a length of 1 meter. The liner is an alumina tube, 7 cm ID and 0.75 meters long. Heat is supplied by a three zone, 4000 watt, 230 volt Thermocraft furnace, with a heated length of 47 cm. The furnace temperature is

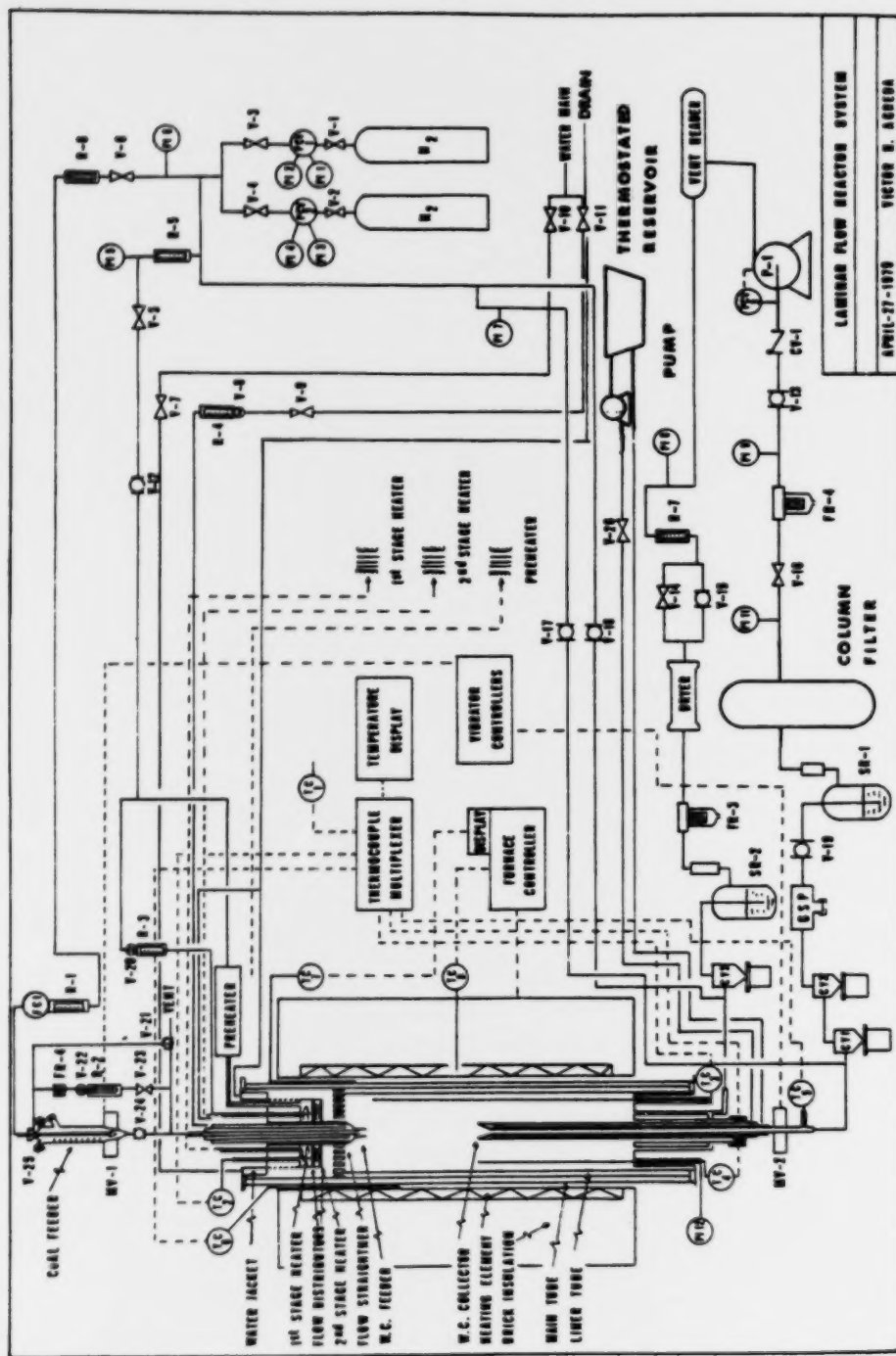


Figure 2.1 Laminar flow reactor system

controlled with a Lindberg Model 59344 digital control console using a Platinel II thermocouple as the sensing element. The thermocouple is located just outside of the heating element in the center of the furnace. The maximum operating temperature is about 1200°C. The temperature profile in the furnace is monitored by two thermocouples connected to a digital temperature display (Omega Model 250). One thermocouple is placed at the top of the reaction zone, close to the feeder top, and the other is placed in the middle of the reactor. The reactor pressure is monitored with an Air Products 0-30 psig (0-1600 mm Hg) gauge.

Nitrogen, used as the main carrier gas, is heated in three stages. The gas is first passed through a preheater (800 watt-19 mm Sylvania serpentine fluid heater) and then is introduced into a two-stage heater in the reactor head. The heater consists of two ARI 1000-watt heating coils separated by a 3.2 mm sintered stainless steel disc, and is encased in a stainless steel shell. These heaters are packed with stainless steel wool to improve the heat transfer efficiency to the gas. The power supplied to the heaters and the preheater is controlled with three variable transformers. A second sintered disc uniformly distributes the gas flow leaving the second stage of the gas heater. A 12.7 mm thick, 1.6 mm bore size alumina honeycomb disc placed 38 mm below the flow distributor and resting on the liner functions as a flow straightener.

In the operation of the device, a small carrier flow of cold gas carries the size-graded, finely ground coal from the feeder-hopper into the preheated nitrogen stream passing downward through the vertical furnace tube in laminar flow. The furnace tube is held at the same temperature as the preheated main gas. The small carrier gas flow mixes rapidly with the hot gas stream, thus allowing the particles to be brought rapidly to the furnace temperature.

Coal particles travel in a narrow laminar flow streamline along the axis of the furnace and are aspirated into a water-cooled collector. The collector has a tapered entry so that the aspirated gases are accelerated to a high-velocity turbulent flow. The consequently high heat transfer rates between the gas and collector wall lead to rapid cooling of the gas and quenching of the devolatilization reactions. Adjusting the distance between the feeder and the collector and adjusting the main gas flow rate can vary the residence time from 50 to 2000 milliseconds. The temperature of the furnace and gas stream can be adjusted up to 1000°C. The pressure of the furnace can be adjusted from atmospheric to 0.4 atm. (gauge).

Feeder Subsystem

The coal feeder employs a mechanical vibrator and partial fluidization of coal particles to get uniform feed rates. The feeder is made of lucite, allowing the coal level and the feed rate to be checked visually. The tube has an outer diameter of 3.8 cm and a coal capacity of about 25 grams. A small stream of carrier gas is injected radially through four equally-spaced holes at the tip of a hollow needle valve. The gas fluidizes the coal particles locally, thus preventing packing and clogging. An external

electric vibrator (VM-1) agitates the entire feeder assembly.

Approximately 50 cm³/min of the feeder carrier gas rises through the hopper, partially fluidizing the bed. The remainder of the gas flows downwards through V-24 (Figure 2.1) carrying the coal particles into the feeder. The fluidizing gas joins the carrier gas stream through V-23. The fluidizing gas is filtered through Fr-4 and metered by R-2. V-21 is a three-way valve used to equalize pressure across the hopper during the startup. For further details on the operation of the feeder system, see Agreda (1979).

Coal particles, now well dispersed in the carrier gas, are injected into the reactor through a water-cooled feeder made of several concentric 316 stainless pipes. The two outer shells have fiberfrax insulation between them to prevent excessive cooling of the main gas. The inner tube is 3.3 mm ID and the outer shell is 2.54 cm OD. The end of the water-cooled feeder is threaded to allow alumina tips to connect it with the 5 mm OD inner tube. The feeder tip is below the bottom of the honeycomb. Several feeder tips with orifice sizes ranging from 1.6 mm to 6.4 mm are available. The velocity of the feeder gas can therefore be varied by changing the gas flow, or, for a given carrier gas flow, by changing the feeder tip bore size. The maximum bore size attainable is that of the thread itself (7 mm). This bore size was used for all the runs in this study.

The feed rate of coal particles is varied by adjusting V-25, the vibrator strength, or the flow rate of fluidizing overflow gas. Coal feed rates between 0.1 g/min and 1.5 g/min can be obtained with reasonable uniformity. In most runs, feed rates were in the range 0.3-0.5 g/min.

Char Collection Apparatus

One of two concentric stainless steel collectors is used to collect the char particles following pyrolysis. One collector, 76.2 cm long with 19 mm OD and 4.6 mm ID, is used to collect low-swelling char (NB8). The mouth of the collector is tapered, decreasing from 18.5 mm to 4.6 mm over a distance of 1.3 cm, so that the mouth makes a 62° angle with a horizontal line at the base. The other collector, 68.6 cm long with 19 mm OD and 7.9 mm ID, is used to handle caking coal (WK11). The angle of the mouth of the collector is again 62°. An electromagnetic vibrator (VM-2) is used at the bottom of the collector to prevent char particles from sticking to the collector walls.

The temperature of the exit gas passing through the collector is monitored with thermocouple TC-5. A thermostatted reservoir (Temtrol 151) from Precision Scientific Company combined with a water pump (Figure 2.2) is used as the water cooling supply to the collectors. The temperature of the reservoir is controlled between 90 and 100°C. The hot water cooling system prevents tars from condensing on the chars which would seriously affect the precision of the estimates of weight losses. This was a problem in early studies performed on the system; the suggestion to use hot water was originally made by Agreda (1979).

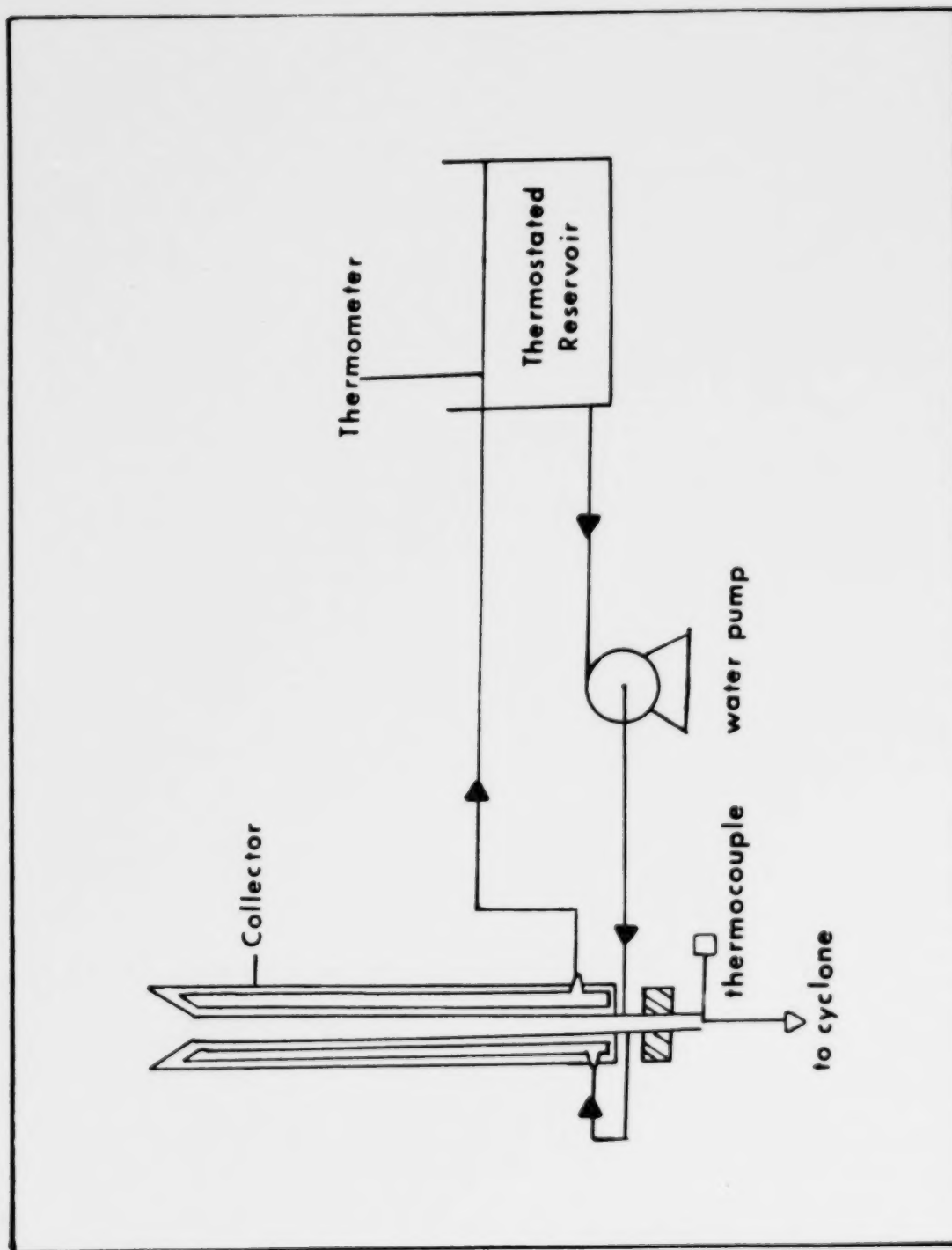


Figure 2.2 Collector hot water cooling system

Char particles in the exit gas are separated in two high efficiency cyclones in series, one 19 mm cyclone and the other 13 mm, both manufactured by the Air Correction Division of Universal Oil Company. Almost 99% of the char particles greater than 10 μ m in diameter can be collected in these two cyclones.

The char that misses the water-cooled collector leaves the reactor through two ports located at the collector support base, and is separated from the exit gas with an Air Correction 13 mm cyclone (CY-3).

Exhaust and Suction Subsystem

The collector suction line is connected to a high flow rate Lamert 03121 vacuum pump. Two water scrubbers, a large surface area filter, and a wool-filled column filter are used to clean the gases leaving the cyclones. The water scrubbers are necessary because the large amount of tars produced must be removed before venting the gas. A Drierite drying column is used to remove moisture before the gases enter the exhaust rotameter, R-7. Three-eighth inch OD stainless steel tubes are used to connect these cleaning units.

Wide-scale Fisher and Porter rotameters accurate to within 1% of full scale are used to measure gas flows throughout the reactor system. Gas flows other than those flowing throughout the reactor system are measured with small Air Products or Matheson rotameters.

Gas Supply and Utilities Subsystems

The nitrogen gas supply consists of two A size nitrogen cylinders fitted with regulators (PCV₁ and PCV₂), and piped such that the supply can be switched from one cylinder to the other during a run without changing the run conditions. City water is used for cooling in the feeder water jacket. One 20 amp, 208 v line and one 20 amp, 110 v line provide electrical power for the equipment.

EXPERIMENTAL PROCEDURE

The following summary briefly states the procedure of the LFR experiments:

1. Set up cooling water and gas supplies.
2. Start cooling water circulation.
3. Set up the hot water cooling system for collector.
4. Wait until the hot water in the cooling system reaches its set

temperature (90°C - 100°C).

5. Heat reactor to desired temperatures as measured by T_3 (the thermocouple at the top of reactor).
6. Load coal in the hopper. Purge with nitrogen.
7. Start gas flow and suction system.
8. Start heater and heat gas until T_2 returns to the desired run temperature.
9. Start coal flow and maintain near 0.4 g/min.
10. Maintain steady-state operation by keeping reactor temperature, pressure, and flow rates constant.
11. Gather data on flows, pressures, temperatures, and levels every 10 minutes throughout the run.
12. Shut off feeder system when feed hopper is empty.
13. Turn off heaters.
14. Turn suction system off.
15. Wait until the temperature reading T_2 (the distributor temperature) is below 400°C and then stop the gas flows.
16. Collect chars from cyclone hoppers and weigh them.
17. Clean up and reset system.
18. If no more runs, turn cooling water off when the entire reactor system is below 50°C .

SECTION 3

DESIGN CALCULATIONS AND DATA REDUCTION EQUATIONS

It is necessary to know the temperature-time histories of the injected coal particles in the laminar flow reactor to be able to interpret the devolatilization data. Although the experimental system was designed to give well-defined wall and gas temperatures in one-dimensional flow fields, the injection of coal particles through a water-cooled feed nozzle makes the actual temperature and velocity fields relatively complicated.

In a previous study (Agreda et al., 1979), formulas were developed to estimate the temperature-time histories from fundamental transport phenomenological considerations. The detailed equations will not be repeated in this volume; the principal results are summarized below.

1. The feeder tip is positioned far enough below the flow straightener to assure a flat gas velocity profile over the entire path from the injector to the collector.
2. There are three concentric annular regions at the tip of the feeder: the emerging jet, a cold boundary layer, and the hot main gas. Expressions are given for the thermal and velocity boundary layer thicknesses and the temperature and velocity profiles within these regions.
3. The velocity of the coal particles is taken to be the sum of the main gas stream axial velocity and the terminal particle settling velocity. The former quantity is that of a fluid in developing laminar flow. The time required for the coal particles to decelerate from the velocity at the feeder tip to their terminal velocities in the reactor is estimated to be roughly five milliseconds or less, negligible compared to typical residence times in the reactor.
4. The residence time of the coal particles in the reactor is obtained by averaging the velocity calculated as above over the distance from the injector to the collector, and correcting for anisokineticity.
5. The time constant for heating the coal particles from the feed temperature to the main gas temperature is estimated from formulas derived by Kobayashi (1976), who obtained them from solutions of the mass, energy, and momentum balance equations for a laminar flow reactor of design similar to that used in the present study, and modified by Agreda (1979).

6. The pyrolysis reactions are quenched in the water-cooled collector in a matter of milliseconds, so that post-reaction effects may be neglected.

DEFINITION OF CONCENTRATION VARIABLES

Coal is divided into four major fractions for the purpose of this study: Moisture (M), ash (A), volatiles (V), and fixed carbon. The elements in coal can be expressed as a weight fraction by the following equation:

$$X^+ = \frac{\text{weight of element in char}}{\text{as received weight of char}}$$

Because the moisture and ash content in the same coal may change slightly from sample to sample, and the moisture of a given sample may even change depending on the environmental conditions to which the sample is subjected, it is sometimes advantageous to express the weight fractions of coal components on moisture-free (m.f.) and dry-ash-free (d.a.f.) bases, in addition to the as-received basis. For the sake of simplicity, the following nomenclature is used: superscript "+" denotes as-received mass fraction (i.e., including moisture and ash); superscript "=" denotes moisture-free mass fraction; and superscript "*" denotes dry-ash-free mass fraction. The mass fractions calculated on different bases are related to one another as follows:

$$X = \frac{X^+}{1 - M^+}, \frac{\text{weight of element}}{\text{weight of dry char}}; \quad (3.1)$$

$$X^* = \frac{X^+}{1 - A^+ - M^+}, \frac{\text{weight of element}}{\text{weight of dry ash free char}} \quad (3.2)$$

$$X^* = \frac{X^=}{1 - A^=}, \frac{\text{weight of element}}{\text{weight of dry ash free char}} \quad (3.3)$$

where M denotes moisture content and A ash content. Throughout this report, subscripts are used as follows: "C" denotes feed coal, "H" denotes char, and "A" denotes ash (e.g., X_H , X_V , etc.).

DETERMINATION OF WEIGHT LOSSES

Since a significant fraction of the char tends to miss the collector mouth or stick to the collector wall in LFR experiments, it is not feasible to determine the weight loss as the difference between feed coal and collected char. If a component in coal is stable throughout the pyrolysis process, this component can be used as a tracer for the indirect calculation of weight loss. The tracer balance on an a.r. basis is:

$$r_C^+ W_C^+ = r_H^+ W_H^+ \quad (3.4)$$

where

r_C^+ = a.r. tracer mass fraction in coal and

r_H^+ = a.r. tracer mass fraction in char.

W_C^+ = a.r. mass of coal

W_H^+ = a.r. mass of char

The fractional a.r. weight loss is given by:

$$V^+ = \frac{W_C^+ - W_H^+}{W_C^+} \quad (3.5)$$

Combining Equation 3.2 with Equation 3.1 yields:

$$V^+ = 1 - \frac{r_C^+}{r_H^+} \quad (3.6)$$

It follows that

$$V^+ = 1 - \frac{r_C^+}{r_H^+} \left[\frac{1 - M_H^+}{1 - M_C^+} \right] \quad (3.7)$$

or

$$V^+ = 1 - \frac{r_C^+}{r_H^+} \quad (3.8)$$

and

$$V^* = 1 - \frac{r_C^+}{r_H^+} \left[\frac{1 - M_H^+ - A_H^+}{1 - M_C^+ - A_C^+} \right] \quad (3.9)$$

or

$$V^* = 1 - \frac{r_C}{r_H} \quad (3.10)$$

or

$$V^* = 1 - \frac{r_C^=}{r_H^=} \left[\frac{1 - A_H^=}{1 - A_C^=} \right]. \quad (3.11)$$

Ash was considered to be the most suitable component for a tracer method technique. Many investigators have used ash as a tracer in determining weight losses (Nsakala, 1976; Kobayashi, 1976; Stickler et al., 1974; Badzioch and Hawksley, 1970). When ash is used as a tracer, Equation 3.37 reduces to

$$V^* = 1 - \frac{A_C^=}{A_H^=} \left[\frac{1 - A_H^=}{1 - A_C^=} \right]. \quad (3.12)$$

Ash content was determined by weighing the residue left after ignition of the coals and chars at 950°C. All the experiments in this study were carried out at 900°C or below.

WEIGHT LOSS ESTIMATION ERRORS

Investigators have reported negative weight loss estimation when the ash-tracer method was used (Badzioch and Hawksley, 1970; Kobayashi, 1976). These findings suggest the ash-tracer method is not an adequate method to estimate weight loss. Kobayashi (1976) and Agreda (1979) have examined in depth the accuracy of the ash-tracer method. Agreda et al. (1979) summarized the possible potential error sources associated with this method:

1. Measured ash contents of the feed coal and the char may be in error either due to analysis errors or to run-to-run variability.
2. The ash contents of coal and char particles vary with particle size. The cyclones used to collect the char particles impose a size classification, and therefore bias the measured ash content of the product. If the cyclone contents are mixed to provide the product char, inhomogeneity and imperfect sampling constitutes another potential source of error.

3. There is a difference between the experimentally measured proximate ash content of an as-received coal and the same coal which has been subjected to predevolatilization.
4. Tar evolved in pyrolysis may condense on the collected char surface, thereby decreasing the apparent weight loss.

Agreda (1979) made four replicate runs in order to determine the effects of chemical analysis errors and run-to-run variability on the determination of weight loss. He used a statistical variance analysis to study these factors, and concluded that the variances in chemical analyses and between runs are not large enough to explain either the magnitude or the trend of the underestimation of weight loss.

Agreda made two room temperature runs to study the second problem. He found the ash content of coal collected in cyclone 1 is less than that of coal collected in cyclone 2 and the weight average ash content of the feed coal. These findings show that samples are not homogeneous or a significant fraction of ash is not collected by either cyclone 1 or cyclone 2. Agreda suggested using the ash content of coal particles processed through the LFR at room temperature instead of using the ash content of feed coal. This can reduce the underestimation of values of weight loss by about 10%.

The findings of Padia (1976) can be used to explain the third problem. Padia concluded that the ash produced from pyrolyzed chars weighs 4.75% less than that produced from unpyrolyzed coal. Padia's findings suggest that the ash-induced error can be minimized by increasing the ash content of the chars by about 5%. Agreda (1979) used this correction factor to reduce the magnitude of the underestimation of weight loss.

Tar condensation on the collected char (the fourth problem) can be noticed visually during the experiments. Yellow-brown fumes of condensing tars deposited on the surface of the chars in cyclone 1 and cyclone 2 diluted the ash content in the char, and contributed to the errors in weight loss estimation. This effect could produce substantial errors in the elemental evolution measurements, especially for mercury and elements predominantly associated with the organic fraction of coal. The effect can be reduced by using a hot water supply to the cooling jacket of the collector (Agreda, 1979). The hot-water cooling system can keep the temperatures of the cyclones at about 100°C, thus keeping some of the tars from condensing.

In this study, all the experiments were carried out with a hot water cooling system, while Agreda (1979) carried out his experiments with a cold water cooling system. The ash contents of NB8 chars from these two systems are compared in Figure 3.1. The significant increase in ash content and better consistency of the data obtained with the hot water system demonstrates the reduction of tar condensation on the collected char.

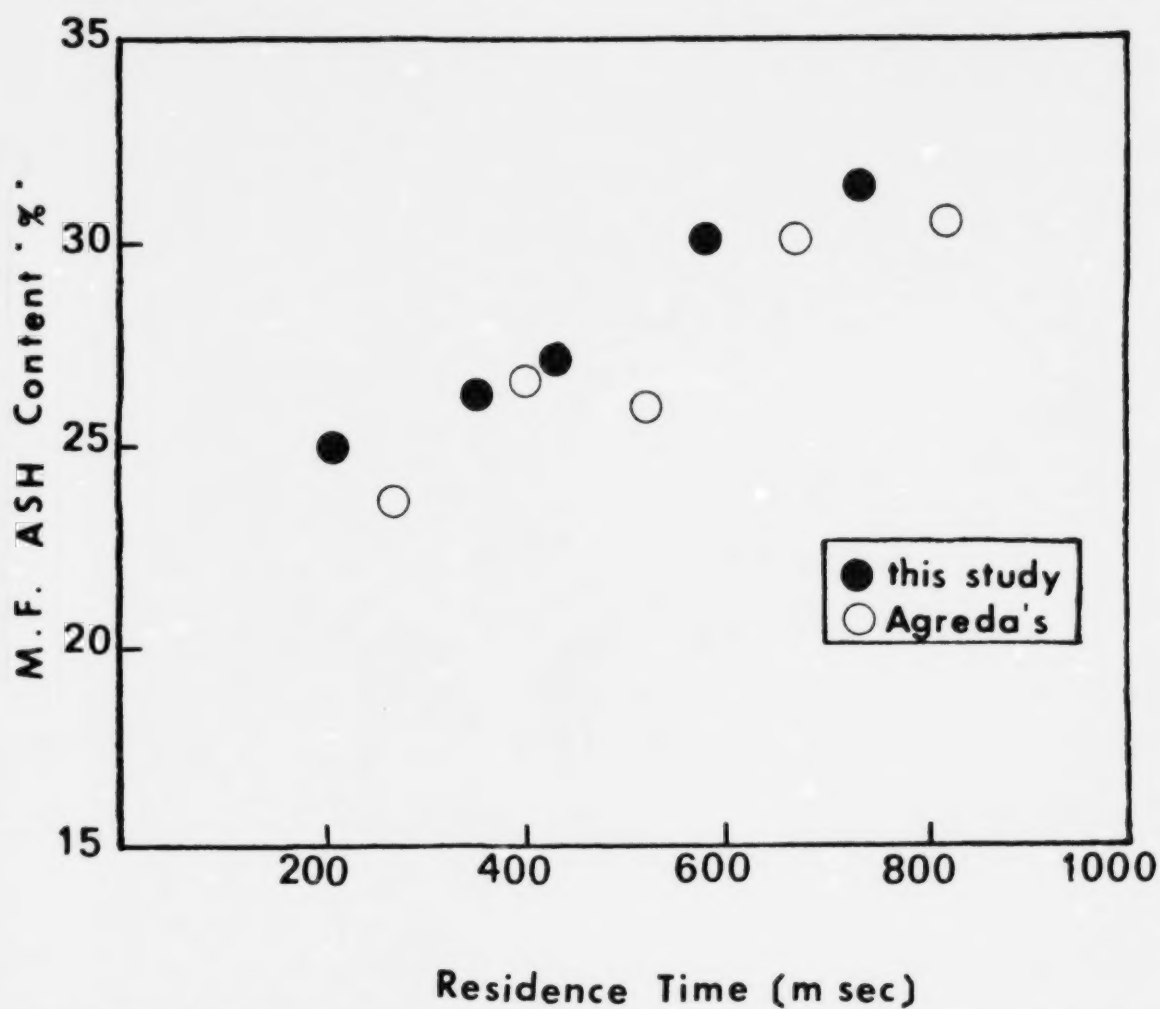


Figure 3.1 Comparison of ash contents of chars from different cooling systems (800° C)

SECTION 4

DEVOLATILIZATION

EXPERIMENTS AND RESULTS

Two coals were pyrolyzed in the laminar flow reactor in this study: North Barber No. 8 (NB8; lowswelling New Mexico subbituminous coal) and Western Kentucky No. 11 (WK11, medium-swelling bituminous coal). Forty-seven runs were carried out. The first twenty-eight runs were made with NB8 coal at temperatures ranging from 500°C to 900°C. A summary list of run conditions is shown in Table 4.1.

The ash tracer technique with a correction applied to account for ash losses was applied to calculate the values of weight loss. The estimated weight losses were then compared with the predictions of five mathematical models (first-order isothermal, Eq. 1.1; Badzioch and Hawksley, Eq. 1.3; Kobayashi, Eq. 1.8; Anthony, Eq. 1.14; and first-order nonisothermal, Eq. 1.17).

Four trace and minor elements (Hg, Pb, As, and S) were analyzed in the chars produced in the laminar flow reactor experiments. Statistical trend analyses of elemental release were performed, and an attempt was made to model the rate and extent of elemental release as functions of time and temperature.

WEIGHT LOSS ESTIMATION

The difficulty in collecting 100% of the char makes it impossible to calculate the weight losses simply by measuring the difference in weight between feed coal and char. Because ash is non-volatile, it can be used as a tracer to estimate weight loss.

It is obvious that for the tracer method to be effective, the tracer (ash) must have certain properties:

1. It must have zero volatility during pyrolysis:
2. It must be homogeneously dispersed throughout the coal and char samples.
3. It must be amenable to accurate analysis.

Table 4.1 Summary of LFR run conditions

Run No.	Coal	T(°C)	t _R (msec)	t _I (msec)	Coal Feed	
					Rate(g/min)	Recovery (%)
8	NB8	500	824.6	726.4	0.30	69.92
9	NB8	500	427.6	329.4	0.375	74.93
10	NB8	500	671.2	573.1	0.30	70.07
11	NB8	500	1145.5	1047.3	0.44	77.40
12	NB8	600	407.4	313.0	0.40	70.61
13	NB8	600	592.8	498.5	0.375	75.02
14	NB8	600	800.5	714.3	0.425	68.95
15	NB8	600	1019.0	924.7	0.49	76.60
16	NB8	700	361.7	271.2	0.343	69.35
17	NB8	700	534.5	443.5	0.30	66.42
18	NB8	700	746.3	655.8	0.30	74.17
19	NB8	700	915.9	825.3	0.40	71.68
20	NB8	550	231.7	135.5	0.432	71.54
21	NB8	550	310.5	214.2	0.50	74.64
22	NB8	550	503.6	407.4	0.38	69.85
23	NB8	550	756.0	659.4	0.45	68.09
24	NB8	550	1074.0	978.5	0.375	70.18
32	NB8	800	210.4	123.5	0.46	66.32
33	NB8	800	352.9	266.0	0.40	67.90
34	NB8	800	434.0	347.1	0.45	61.71
36	NB8	800	578.9	648.1	0.30	59.66
37	NB8	800	735.0	492.0	0.34	59.59
38	NB8	900	207.4	124.0	0.33	65.32
39	NB8	900	347.2	263.7	0.42	61.68
40	NB8	900	473.2	389.7	0.45	60.60
41	NB8	900	473.2	389.7	0.40	58.66
42	NB8	900	581.0	497.5	0.56	57.63
43	NB8	900	724.8	641.3	0.37	55.40
44	WK11	800	196.8	109.8	0.38	54.80
45	WK11	800	334.8	247.9	0.30	42.69
46	WK11	800	446.3	359.3	0.37	55.00
47	WK11	800	845.8	531.2	0.41	46.58
48	WK11	800	618.1	758.9	0.50	46.32
49	WK11	400	292.8	190.6	0.29	76.25
50	WK11	400	653.3	551.1	0.32	81.74
51	WK11	400	980.3	878.0	0.33	70.80
52	WK11	400	1231.2	1231.2	0.42	78.68
53	WK11	600	244.9	150.7	0.38	76.67
54	WK11	600	557.2	463.0	0.37	61.53
55	WK11	600	779.1	683.9	0.34	61.87
56	WK11	600	1034.6	940.4	0.40	63.76
57	WK11	900	202.2	118.7	0.42	47.33
58	WK11	900	413.5	330.0	0.46	45.81
59	WK11	700	271.9	181.4	0.273	56.00
60	WK11	700	970.3	879.8	0.38	59.40
61	WK11	700	493.2	402.7	0.35	52.70
62	WK11	700	711.0	620.5	0.40	56.80

Values of V_A (d.a.f. weight loss), V_A (moisture-free weight loss), and V_A (as-received weight loss) were determined by the ash tracer method using Eqs. 3.4-3.11, and are tabulated by Kau (1980). The results are plotted in Figures 4.1 and 4.2 for NBS coal and WK11 coal. As the plots show, low temperatures and low residence times consistently lead to negative values of V_A . Since negative dry-ash-free (d.a.f.) weight losses are a physical impossibility, it is clear that one or more of the assumptions inherent in the ash tracer method are violated, thus leading to errors in the estimated weight losses.

Corrected dry-ash-free weight losses were estimated in this study following a procedure developed by Agreda(1979):

$$V^* = 1 - \frac{E_C^*}{E_H^*} \quad (4.1)$$

where

E_C^* = d.a.f. ash fraction of particles collected during cold runs and

E_H^* = d.a.f. ash fraction of char particles corrected for Padia's effect.

E_H^* is calculated from the following equations:

$$E_H^* = \frac{E_H^+}{1 - E_H^+ - N_H^+} \quad (4.2)$$

where

$$E_H^+ = \frac{1.0475 A_H^+}{1 + 0.0475 A_H^+} \quad (4.3)$$

$$N_H^+ = \frac{M_H^+}{1 + 0.0475 A_H^+} \quad (4.4)$$

A_H^+ = as-received ash content of char

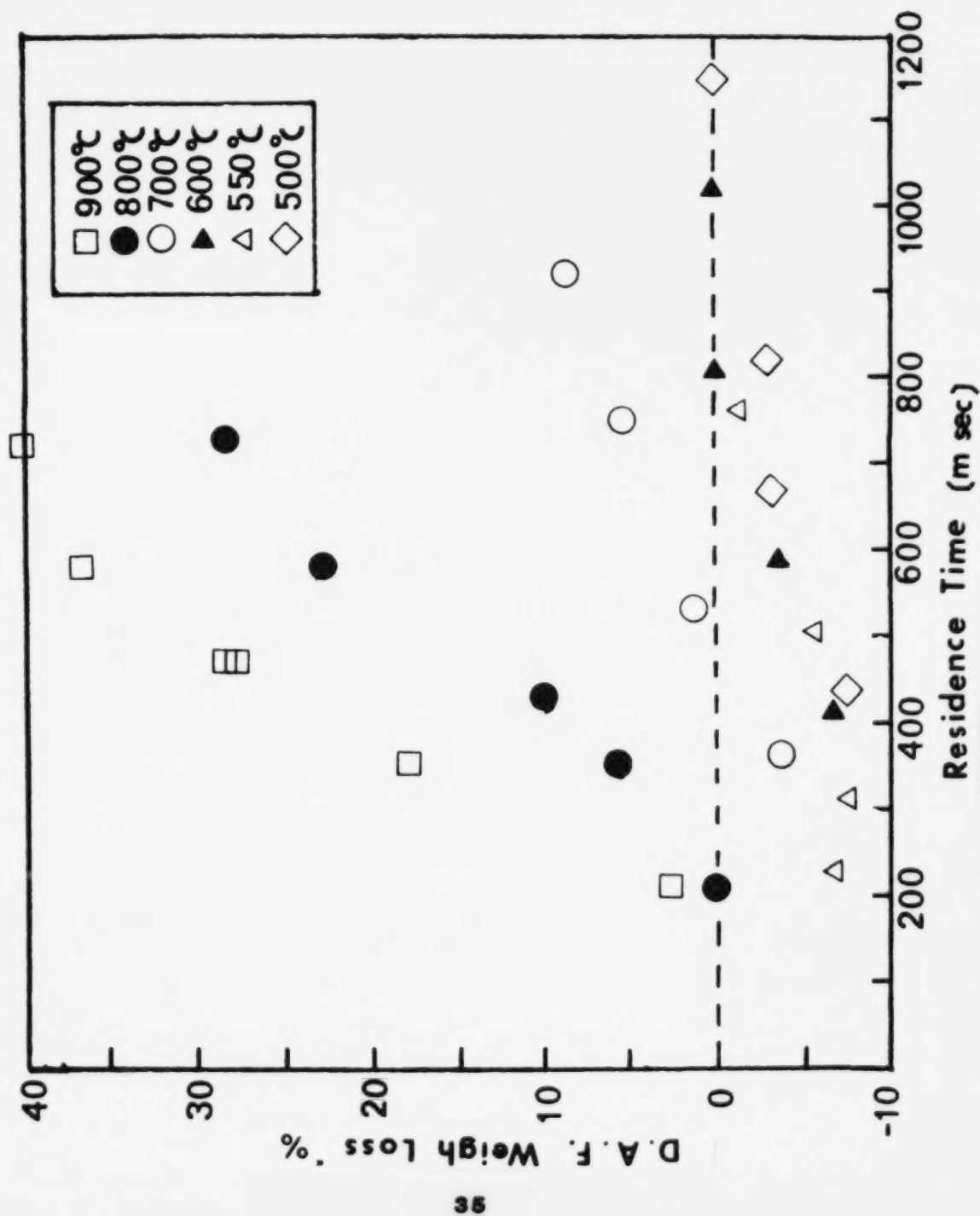


Figure 4.1 Weight loss by ash tracer method---NB8 coal

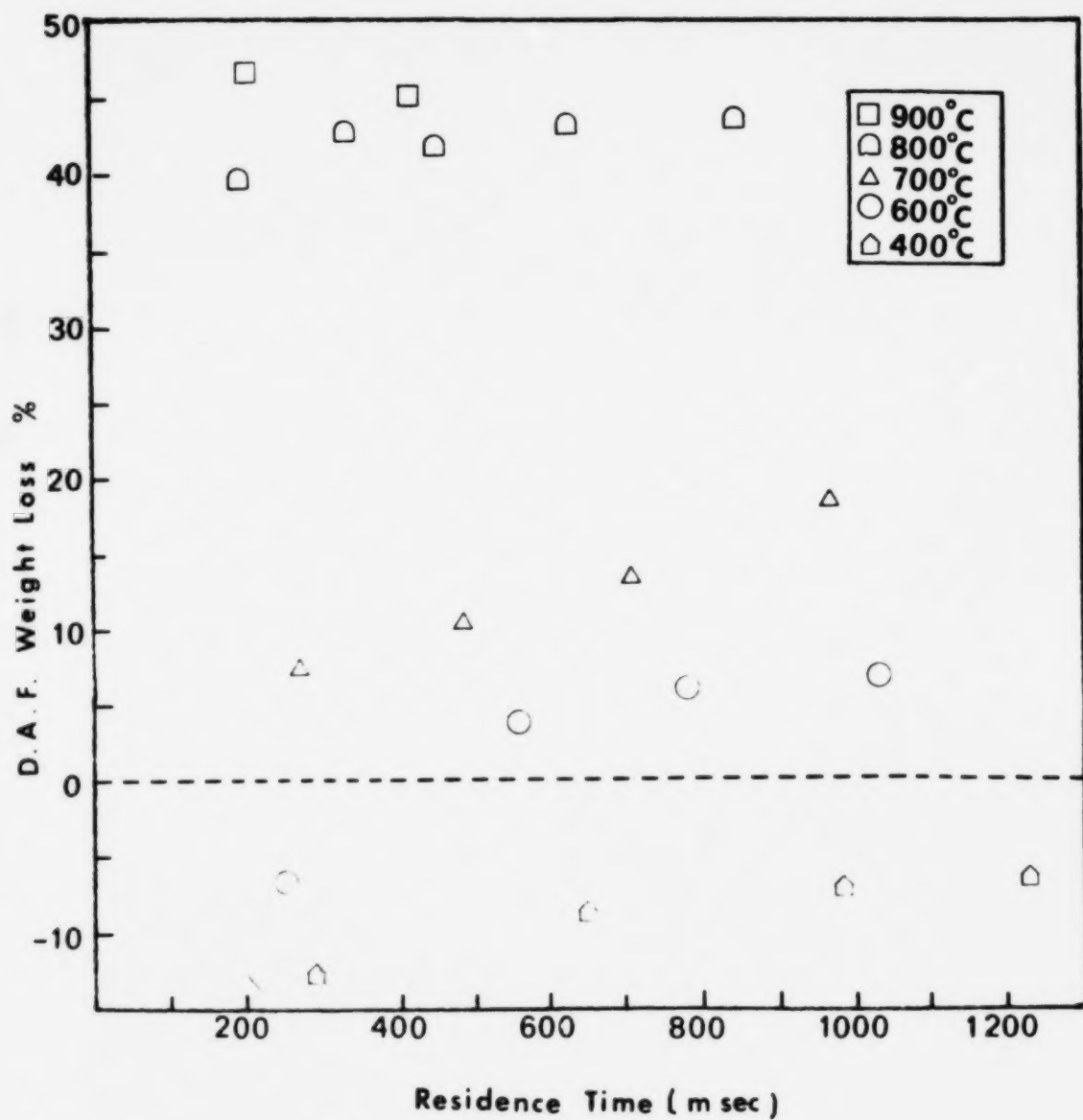


Figure 4.2 Weight loss by ash tracer method--WKII coal

M_H^+ = as-received moisture content of char.

E_H^+ and N_H^+ are the ash and moisture contents that the char would have if the yield of ash had not been reduced by the Padia effect (see Section 3).

Actual moisture and ash contents of the feed coals and chars were used to calculate as-received and moisture-free weight losses from the equations

$$V^+ = 1 - \frac{(1 - V^*) (1 - M_C^+ - A_C^+)}{1 - M_H^+ - A_H^+} \quad (4.5)$$

$$V^+ \text{ (m.f.)} = 1 - (1 - w^+) \left(\frac{1 - M_H^+}{1 - M_C^+} \right) \quad (4.6)$$

Weight loss values calculated in this manner are tabulated by Kau(1980).

The method outlined above provides correction for only chemical and physical ash losses; it does not take into account loss of submicron particles and condensation of tars on the product char. Agreda (1979) proposed a method of specifying lower and upper bounds for weight loss including the effects of these phenomena. Because of the design of the reactor collector base, some of the product char is inevitably not collected in the cyclones. Therefore, the difference between the d.a.f. weight of coal feed and the total d.a.f. weight of the char collected in all three cyclones (V_W^*) can be regarded as the upper bound on weight loss. This quantity can be estimated by the following equation:

$$V_W^* = \frac{[1 - M_C^+ - A_C^+] - R_H [1 - M_H^+ - A_H^+]}{1 - M_C^+ - A_C^+} \quad (4.7)$$

where

$$R_H = \frac{\text{weight of char recovered in three cyclones}}{\text{weight of feed coal}}$$

The lower bound can be taken to be the uncorrected value of V_A^* , which does not account for ash losses.

The weight loss estimates and bounds calculated as described above are shown in Tables 4.2 and 4.3 for NB8 and WK11 coal respectively, and the weight losses are also shown in Figures 4.3 and 4.4 for NB8 and WK11 coals respectively. NB8 (low-swelling coal) exhibited a much lower devolatilization rate than WK11 (medium-swelling coal) at a given

temperature. At higher temperatures, equilibrium is achieved within tens of milliseconds for WK11 coal while NB8 coal takes hundreds of milliseconds to reach equilibrium.

Quantitative comparison of the data obtained in this study with data obtained by other researchers is quite difficult to obtain, for several reasons. The data obtained by each researcher reflects strongly the equipment design and running conditions used (e.g., feeder, main, and suction gas flow rates); residence time calculations and estimations of particle time-temperature histories depend on the model used and the assumptions made; and weight losses estimated by the ash tracer method are dependent on the efficiency of the devices used to collect the char.

It is however, instructive to compare NB8 data from this study with data from the previous study in this research (Agreda et al. 1979), since both were performed on the same experimental system. As shown in Figure 4.5, Agreda's 800°C results are scattered and consistently lower than the 800°C results from the present study. This phenomenon may be due to the use of a hot-water cooling system in the current study, which minimized the effect of tar recondensation on the measured weight losses. However, the 900°C results from both studies are consistent.

MODELING

Experimental weight loss data obtained in this study for NB8 and WK11 coals and data for Montana Rosebud subbituminous coal obtained by Agreda (1979) have been correlated with five models: a single first-order reaction model (both isothermal and nonisothermal reactor operation being considered separately), Badzioch and Hawksley's (1970) isothermal model, Kobayashi's (1976) nonisothermal two-reaction model, and Anthony's (1976) nonisothermal infinite parallel reactions model. For the latter three models, the parameters proposed by the model developers were first used; then, for all models the parameters were adjusted to obtain least-squares fits to the data. In the latter calculations, an initial set of model parameters was chosen, weight losses were evaluated at a series of times and temperatures corresponding to experimental data points, and the unweighted sum of squares of residuals

$$SSE = [V_{exp}^* - V_{model}^*]^2 \quad (4.8)$$

was calculated. Then the model parameters were systematically varied to determine the set that minimized SSE. The algorithms used for this purpose differed from one model to the next and will be discussed in subsequent sections.

Equilibrium Devolatilization

As important parameter of the models is the equilibrium or asymptotic weight loss at the reaction temperature. This quantity can be obtained either from batch pyrolysis data or from long residence time data in the laminar flow reactor. Duhne (1977) has shown that asymptotic equilibrium values for physical and chemical processes can be estimated from an equation of the form

$$V^* = \frac{d}{t_R} + V_f^*, \quad V^* > 0.67V_f^* \quad (4.9)$$

where d = a constant. If V^* is plotted versus $1/t_R$, the plot should approach a straight line at low values of the abscissa with the intercept equal to V_f .

Plots of this type are shown for Montana Rosebud (MRS) subbituminous coal (Agreda et al., 1979) and WK11 coals in Figures 4.6 and 4.7, and the resulting values of V_f are tabulated in Table 4.4, along with batch pyrolysis equilibrium values obtained by Agreda et al. (1979). NB8 coal did not come close enough to equilibrium in the LFR experiments for the given procedure to be used. The batch values shown in Table 4.5 were used for all kinetic modeling for this coal.

The fact that the asymptotic and equilibrium weight loss estimates shown in Table 4.4 differ is not surprising. In the case of the MRS coal, the equilibrium values appear to be higher than the asymptotic values. This result is consistent with the finding of Horton (1979), who reviewed the fast pyrolysis data of several researchers and noted that a quasi-equilibrium is reached before the particles are quenched, but that additional devolatilization occurs when the quenched char particles are reheated in a batch reactor.

Table 4.2 Weight loss estimates and bounds (NB8)

Run No.	V_A^*	V^*	V_W^*
	(Low Bound)		(High Bound)
8	-2.59	6.60	25.06
9	-7.40	2.22	18.71
10	03.03	6.19	24.30
11	-0.10	8.86	17.02
12	-6.46	3.07	23.00
13	-3.21	6.03	19.06
14	-0.29	8.69	26.15
15	-0.29	9.22	18.07
16	-3.20	6.04	24.89
17	1.18	10.03	28.83
18	5.43	13.90	22.34
19	8.83	16.99	26.51
20	-6.74	2.81	22.37
21	-7.21	2.39	18.57
22	-5.20	4.22	25.03
23	-1.43	7.65	26.92
24	0.99	9.85	24.98
32	0.28	9.21	28.74
33	6.06	14.47	28.07
34	10.30	18.33	35.60
36	22.88	29.79	40.35
37	28.46	34.87	41.67
38	2.59	11.31	30.02
39	17.98	25.32	36.89
40	28.33	34.75	40.61
41	27.88	34.34	42.39
42	36.59	42.27	45.68
43	39.87	45.25	48.71

Table 4.3 Weight loss estimates and bounds (WK11)

Run No.	V_A^* (Low Bound)	V^*	V_W^* (High Bound)
44	39.30	44.37	47.80
45	42.38	47.20	53.33
46	41.86	46.72	47.10
47	43.44	48.17	56.02
48	43.07	47.87	56.32
49	-12.74	0.00	22.30
50	-8.48	0.58	16.04
51	-8.88	0.21	27.67
52	-6.61	2.30	20.00
53	-6.25	2.63	22.54
54	4.09	12.10	37.77
55	5.98	13.83	38.00
56	6.89	14.66	35.84
57	46.78	51.23	56.17
58	45.10	49.68	57.37
59	7.48	15.21	44.40
60	18.16	24.99	42.23
61	10.37	17.86	48.35
62	13.63	20.85	43.84

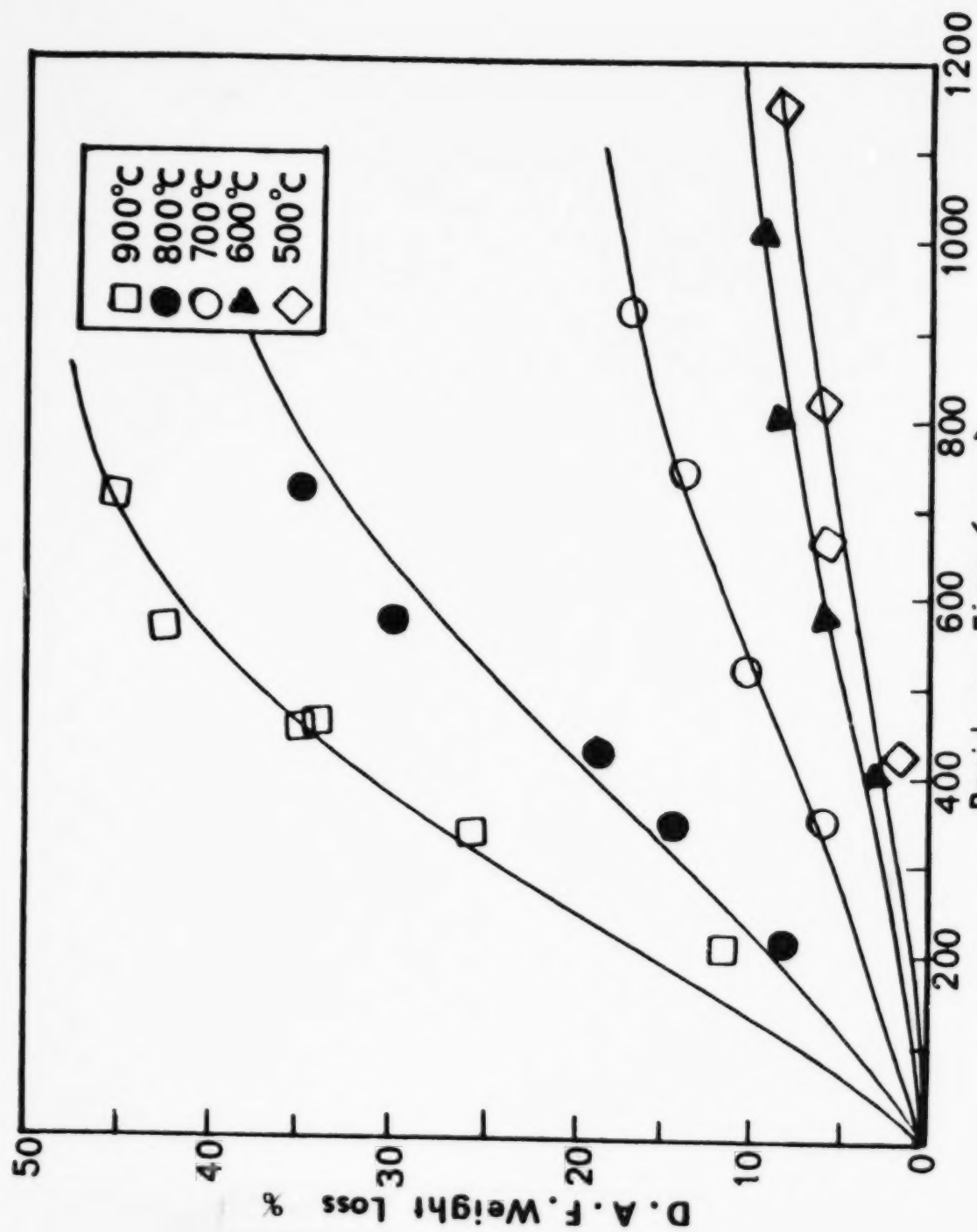
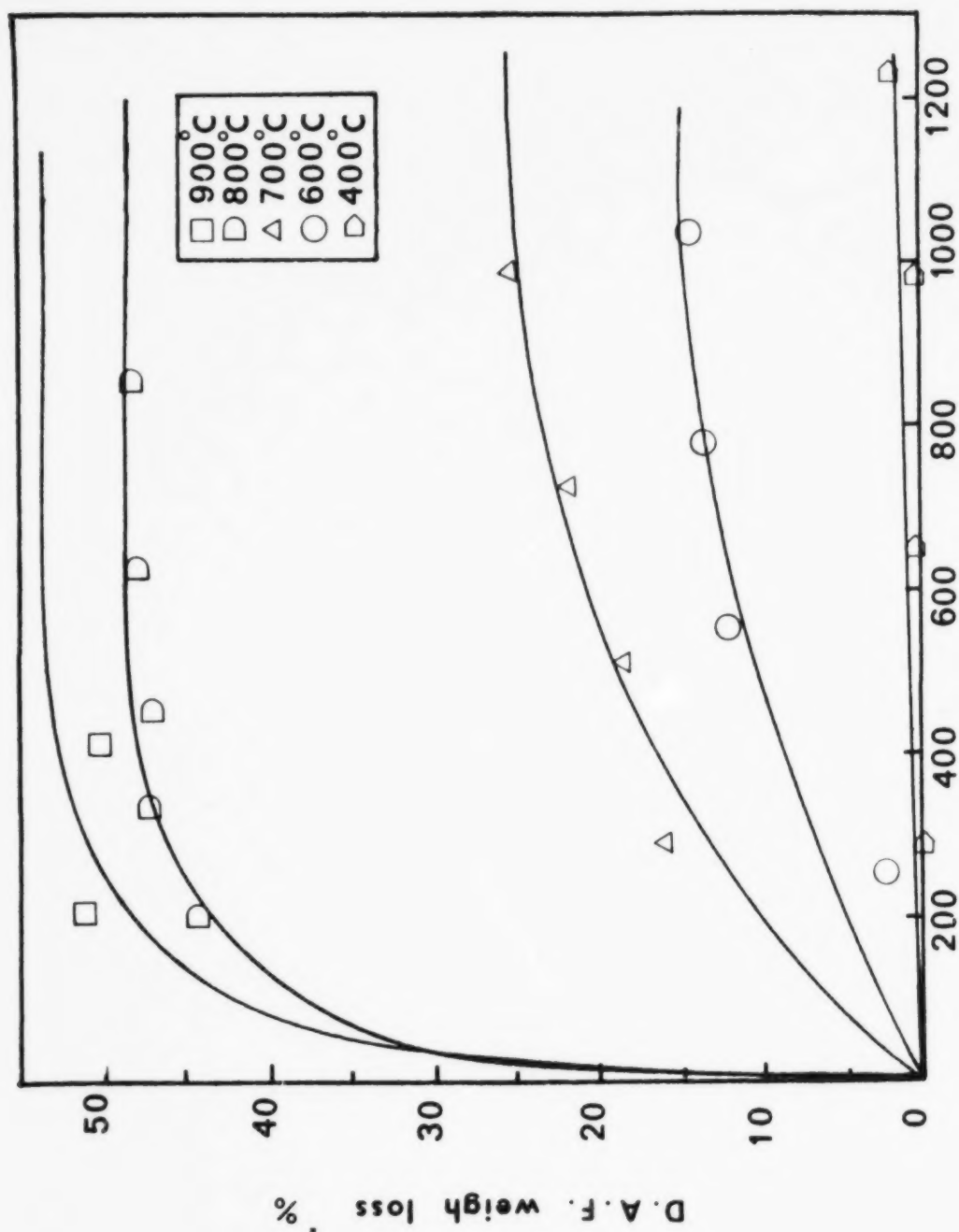


Figure 4.3 d.a.f. weight loss of NB8 coal



Residence Time (m sec)
Figure 4.4 d.a.f. weight loss of WKII coal

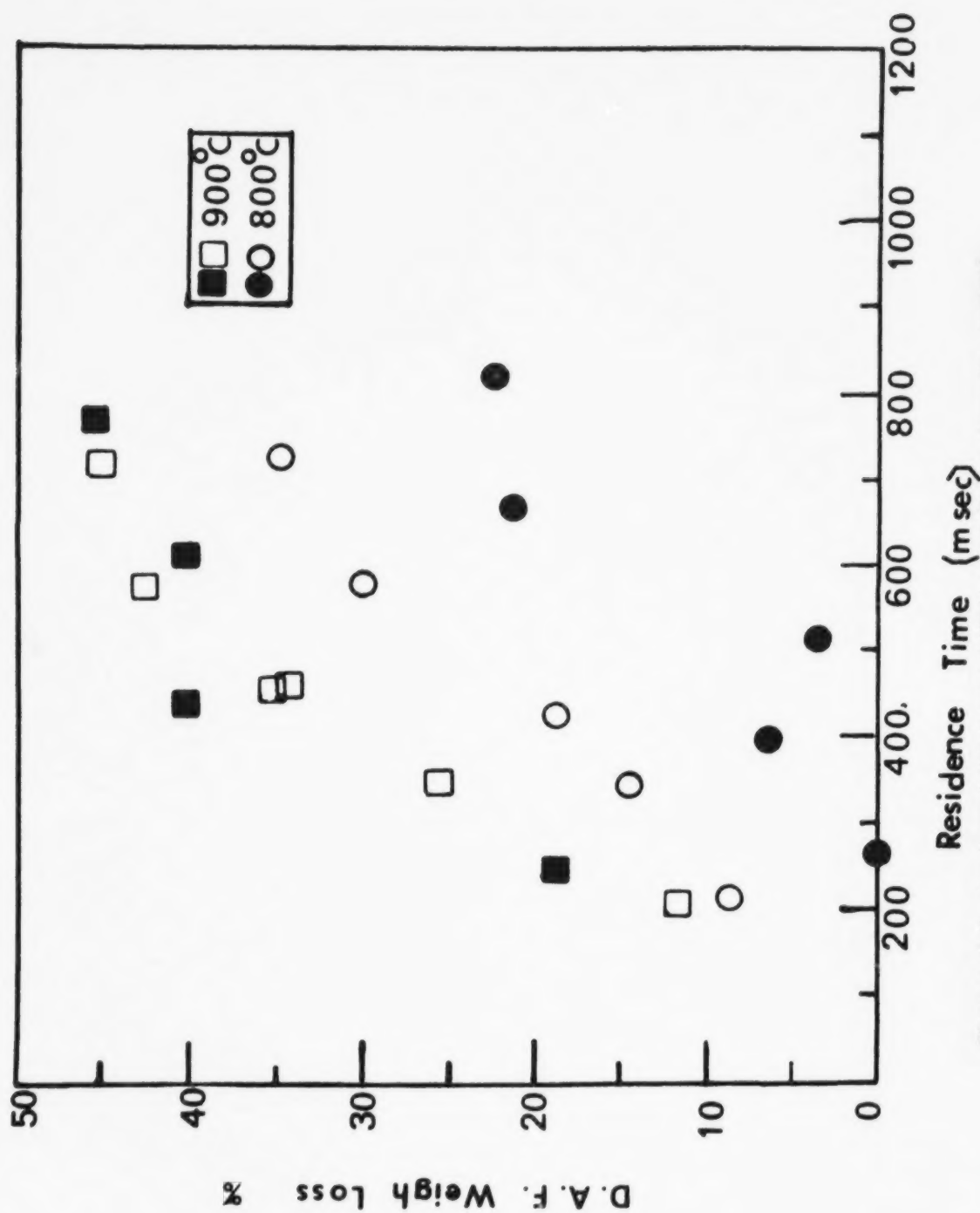


Figure 4.5 d.a.f. weight loss of NB8 coal (from Agreda, 1979)

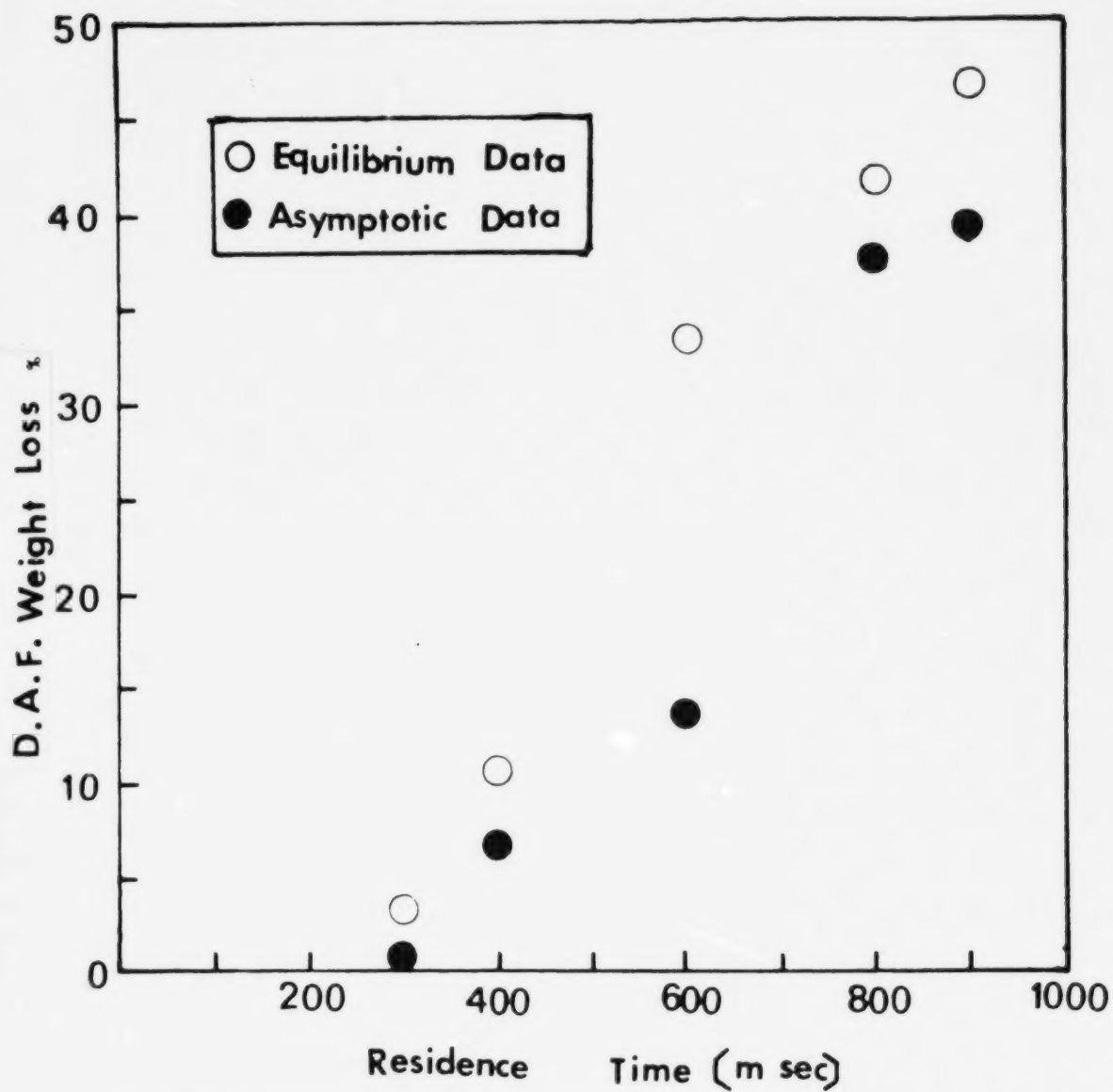


**Figure 4.6 Comparison of LFR asymptotic d.a.f. weight losses with batch equilibrium d.a.f. weight losses (MRS)
(from Agreda, 1979)**

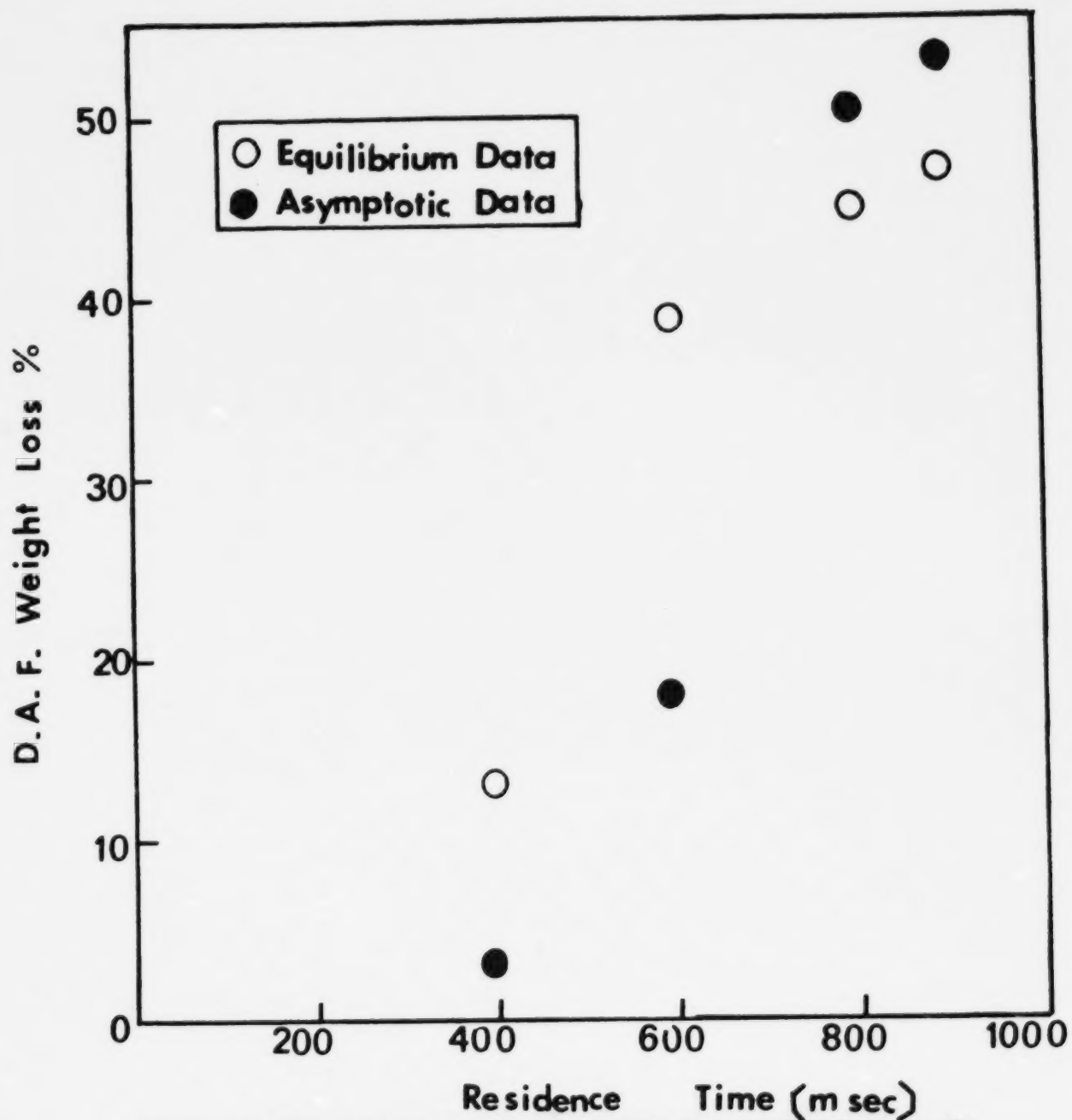


Figure 4.7 Comparison of LFR asymptotic d.a.f. weight losses with batch equilibrium d.a.f. weight losses (WKII)

Table 4.4 Equilibrium and asymptotic d.a.f. weight losses (WK11 and MRS)

Coal	Temperature($^{\circ}$ C)	Asymptotic(0)	d.a.f.Weight
		Equilibrium(X)	$V_f^{* \text{ Loss}}$ (%)
WK11	400	0	2.94
		X	12.94
WK11	600	0	17.65
		X	38.76
WK11	800	0	49.90
		X	44.67
WK11	900	0	52.90
		X	46.50
MRS	300	0	0.85
		X	3.27
MRS	400	0	6.76
		X	11.63
MRS	600	0	13.44
		X	33.42
MRS	800	0	37.4
		X	41.73
MRS	900	0	39.27
		X	46.85

In the case of the WK11 coal, the equilibrium values stay higher than the asymptotic values at temperatures lower than 700°C. This can be explained by the caking characteristics of this coal. Caking coals often devolatilize with the formation of bubbles and then resolidify during batch pyrolysis, while in fast pyrolysis the structure of the coal particles is deformed as the volatile matter is removed. Therefore, after caking (about 700°C), the fast pyrolysis asymptotic weight losses should be higher than the batch pyrolysis equilibrium values.

The values of V_f^* determined above (from the LFR measurements for MRS and WK11 and from batch measurements for NB8) were fitted versus T with a fourth-order polynomial:

$$V_f^*/100 = B_0 + B_1T' + B_2T'^2 + B_3T'^3 + B_4T'^4 \quad (4.8)$$

where $T' = T(^{\circ}\text{C})/100$. The coefficients of this polynomial for the three coals are shown in Table 4.6.

Single First-Order Reaction Model: Isothermal Case

The following model equation was fit to results obtained for all three coals:

$$V = V_f^* [1 - \exp(-Kt_I)] \quad (4.9)$$

where

$$K = B \exp(-E/RT) \quad (4.9a)$$

$$t_I = t_R - 3t_H \quad (4.9b)$$

The heating time constant, t_H , is determined as discussed in Section 3. Equation (4.9b) is an empirical formula proposed by Agreda(1979).

The values of the parameters (B , E) and the minimum values of SSE determined by linearization and linear regression are shown for all three coals in Table 4.7.

Table 4.5. Equilibrium d.a.f. weight losses (NB8)

Temperature (°C)	d.a.f. Weight Losses (%)
300	3.27
400	11.63
600	33.42
800	41.73
900	44.23

Table 4.6 Coefficients of the fourth-order polynomial for asymptotic weight loss.

Coal	B_0	B_1	B_2	B_3	B_4
MRS	-1.783	1.1411	-0.2590	0.02479	-0.0008233
WK11	-4.291	2.691	-0.5927	0.05477	-0.001775
NB8	1.052	-0.7150	0.1615	-0.01367	0.0004044

Table 4.7 First-order isothermal devolatilization model parameters and sums of squares of residuals

Coal	E_0 (kcal/mol)	B_0 (s ⁻¹)	SSE
NB8	11.3	353	397
MRS	3.35	10.0	413
WK11	14.2	6320	597

Single First-Order Reaction Model: Nonisothermal Case

The model equations, originally given in Section 1.2.4, are

$$V^* = \frac{\int_0^{t_R} dt K(V_f^*) \exp(\int_0^t K dt)}{\exp(\int_0^{t_R} K dt)} \quad (1.19)$$

where $K[T(t)]$ is again given by Equation (4.9a). Initial estimates of the parameters B and E were obtained by assuming isothermality and applying the linear regression method described above. Then the true temperature-time relationship for the reactor (calculated by the procedure outlined in Section 3) was substituted in the Arrhenius expression for $K(T)$, and a Pattern Search function minimization algorithm (Beightler et al., 1967) was used to find the values of B and E that minimize the function SSE of Equation 4.8. The results are shown in Table 4.8 and again in Tables 4.12-4.14.

Table 4.8 Single first-order reaction nonisothermal devolatilization model parameters (NB8, WK11, MRS) and sum of squares of residuals

Coal	E_0 (kcal/mole)	B_0 (1/sec)	SSE
NB8	18.2	7853	154
MRS	18.4	7677	242*
WK11	16.0	19100	439

Badzioch-Hawksley Model

The model equation for the dry ash-free weight loss (Eq. 1.3) was first fit to experimental results (equilibrium or asymptotic values) at different temperatures for all three coals to obtain the parameters (K_1 , Q , K_2). Values of these parameters determined by using Marquardt's (1963) nonlinear regression algorithm were then substituted into Equation 1.3 to estimate the parameters A and B . The values of parameters A and B and the minimum values of SSE determined by applying the same algorithm are shown in Table 4.9, along with the calculated values of K_1 , K_2 , and Q . The values of t_1 (isothermal residence time) were calculated from Eq. 4.9b.

Table 4.9 Badzioch and Hawksley devolatilization model parameters and sum of squares values

Coal	Q	K_1	K_2	A	B	SSE
WK11	1.8	1.938×10^{-3}	676.71	6.096×10^7	1.63×10^4	513
NB8	1.2	2.55×10^{-3}	470.81	4335	8379	134
MRS	1.8	1.03×10^{-3}	589	906.3	6366	194

Theoretical Comparison of Anthony and Kobayashi Models

Two currently used models for devolatilization are those of Anthony (1974) and Kobayashi (1976). Before proceeding to correlations of the data obtained in this study, it may be instructive to consider the bases of these two models. They differ in several respects:

1. Anthony postulates an infinite number of parallel first-order reactions, with a common frequency factor for all rate laws and a Gaussian distribution of activation energies. Kobayashi postulates two parallel first-order reactions, with different stoichiometric extents, frequency factors, and activation energies for each reaction.
2. Anthony's model has three adjustable parameters: the frequency factor and the mean and standard deviation of the Gaussian distribution of activation energies. However, indications are that the model is relatively insensitive to the value of the frequency factor, so that

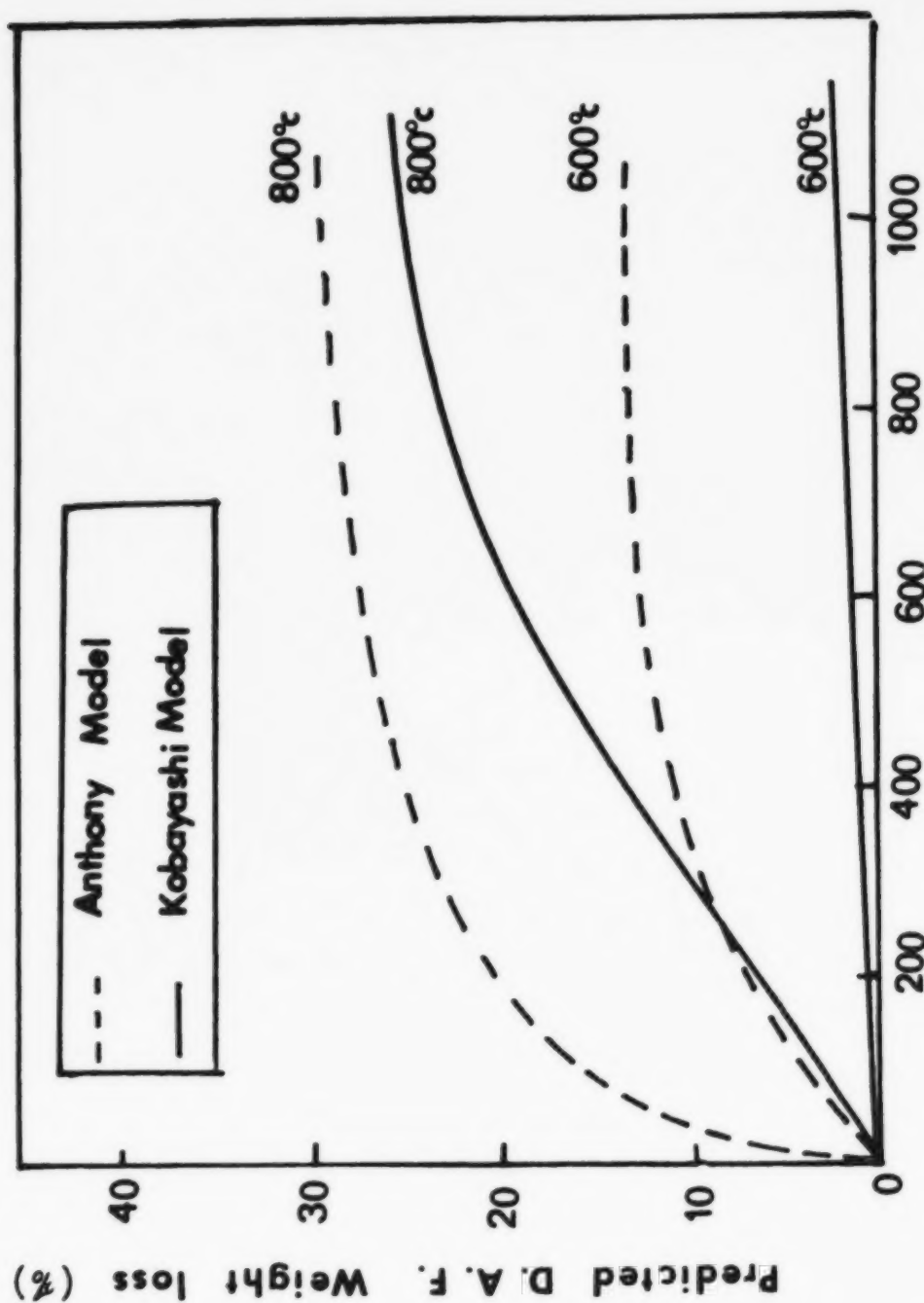
this parameter may be set to an arbitrary value, and the fitting performed by adjusting only two variables. Kobayashi's model has six adjustable parameters: two stoichiometric extents, two frequency factors, and two activation energies.

3. The data on which Anthony's model was based were obtained in an electrically heated wire grid reactor, and experiments carried out by Suuberg (1978) that appeared to confirm the validity of the model were performed on the same type of apparatus. The difficulties associated with this approach are :

- (i) The uncertainty of the heating time. When coal is heated to a specified temperature, there is always a time lag between the point at which heating begins and the point at which the coal reaches the specified temperature.
- (ii) A low cooling rate. After the heater is turned off, the sample remains in the reactor and cools at a rate 10^2 - 10^3 °C/s⁻¹ for a few seconds. During this period, some volatile matter may be evolved from the char particles, resulting in a higher weight loss.
- (iii) Resolidification of volatile matter. Since this is a stationary reactor, some of the volatile matter released may repolymerize and deposit on the char.

On the other hand, Kobayashi's experiments were performed in a laminar flow reactor, similar to the one used in the present study. The problems that arise in experiments of this type--ash loss errors, tar recondensation on the collected char, etc.--have been summarized previously. The principal advantage offered by the LFR is a precise control over residence time and extremely low heating and quench times compared to those characteristic of the heated grid.

A comparison of the predictions of both models is shown in Figure 4.8 and Table 4.10. A coal with the properties of Montana Rosebud subbituminous is used as the basis of comparison. Devolatilization curves predicted by both models are shown for 600°C, corresponding to a relatively low pyrolysis temperature, and 800°C, a moderate-to-high temperature. The model parameters are those suggested by Anthony (1976) and by Kobayashi (1976), and are as follows:



Residence Time (m sec)

Figure 4.8 Comparison of model predictions (MRS)

Table 4.10 Comparison of Anthony and Kobayashi model predictions

T (°C)	t_R (msec)	v^* (Kobayashi)	V^* (Anthony)
600	172.0	0.280	5.430
600	284.8	0.658	9.656
600	521.8	1.398	11.511
600	773.5	2.148	12.917
800	171.1	4.708	19.653
800	270.0	9.238	22.596
800	518.8	17.716	16.211
800	770.1	23.254	28.411
800	825.0	24.319	28.843

Anthony

$$V_f^* (1000^\circ\text{C}) = 47\%$$

$$B(\text{s}^{-1}) = 1.0 \times 10^{10}$$

$$E_0 (\text{kcal/mol}) = 48.7$$

$$s(\text{kcal/mol}) = 9.5$$

Kobayashi

$$a_1 = 0.3$$

$$a_2 = 1.0$$

$$B_1 = 2 \times 10^5$$

$$B_2 = 1.3 \times 10^7$$

$$E_1 = 25$$

$$E_2 = 40$$

The predictions of the two models are seen to be quite different. Anthony's model predicts that equilibrium is reached in a few hundred milliseconds while Kobayashi's model predicts an increasing trend even at long residence times. At all temperatures, Anthony's model predictions are consistently above Kobayashi's model predictions.

The observed differences are consistent with the previous observations regarding the two models. Anthony let his coal samples remain in the heated grid reactor for a few seconds after the heater was turned off. Therefore, his weight loss values should reach equilibrium during this period of time and stay higher than those of Kobayashi.

Kobayashi Model

The model equations are given in Section 1 as Eqs. 1.8-1.10. The asymptotic value of V_f^* under isothermal conditions is given by

$$V_f^* = \frac{a_1 K_1 + a_2 K_2}{K_1 + K_2} \quad (1.10)$$

As indicated by Kobayashi (1976), a_1 and a_2 are the asymptotic values of weight loss at low and high temperatures respectively; hence a value of $a_2 = 1$ can be assigned, as complete weight loss is expected at high temperatures. Kobayashi used a fixed value of a_1 for all temperatures. An alternative is to set a_1 equal to the asymptotic weight loss calculated from Equation 1.20. This must lead to some error, since this quantity is in fact given by Equation 4.13; however, the error is not excessive, and to be more precise would impose an unnecessary degree of complexity in the modeling.

The asymptotic weight losses calculated using a fixed value $a_1 = 0.3$ (the value used by Kobayashi) and floating a_1 values coupled with Kobayashi's model parameters in Equation 4.13 are compared in Table 4.11 with measured asymptotic weight losses for WK11 coal. As shown in this table, a fixed value of a_1 results in an extremely poor prediction of asymptotic weight losses at different temperatures. Therefore, the fourth-order polynomial (Equation 1.20) was used to calculate values of a_1 .

Kobayashi determined his model parameters as follows. He first assumed a single first-order reaction and calculated the apparent activation energy (25 kcal/mole) for the first-order rate constant. This value he designed as E_1 . He then fixed this value and performed a least squares search to determine the best values of E_2 , B_1 , and B_2 . The value of E_2 determined in this manner was 40 kcal/mole.

In the present study, the value of E_1 for each coal was taken to be that determined by fitting the nonisothermal single first-order reaction model to the weight loss data, and the value of E_2 was arbitrarily taken to be 40 kcal/mole. Then, values of the other two parameters (B_1 and B_2) were determined with a Pattern Search function minimization algorithm. The parameters estimated in this manner and Kobayashi's parameters are shown in Tables 4.12, 4.13, and 4.14 along with the SSE values for all the three coals.

Kobayashi's model predictions obtained using his original parameters are compared with the model predictions obtained using the fitted parameters and floating a_1 values for NB8 coal in Figure 4.9 and Table 4.15. Kobayashi's original model predictions at 800°C and 600°C are consistently lower than the experimental data. On the other hand, Kobayashi's model predictions with fitted asymptotic weight losses show good agreement with the data.

The fit of the model to the MRS data is seen to be significantly better for the fixed a_1 rather than the floating a_1 when Kobayashi's model parameters are used. On the other hand, the fit of the model to NB8 and WK11 data is seen to be better for the floating a_1 value rather than the fixed a_1 value when the same parameters are used. None of the fits is particularly good, however, and substantial improvements are obtained by adjusting the parameter values from the values proposed by Kobayashi. This point will be discussed subsequently.

Anthony Model

The model equations are given as 1.14 and 1.15 in Section 1. The values of V^* were calculated using the same fourth-order polynomial (Equation 1.20) used in the single first-order model for different temperatures and the calculated values were substituted in Equation 1.14. The temperature-time relationship for the reactor (calculated by the procedure outlined in Section 3) was also substituted into Equation 1.14.

Table 4.11 Comparison of measured asymptotic weight losses with losses predicted using fixed and floating a_1 values

T(°C)	Measured	V_f^* (%)	predicted
		predicted $a_1 = 0.3$ $a_2 = 1.0$	$a_1 = V_f^*(\text{exptl})$ $a_2 = 1.0$
600	17.65	30.80	18.58
700	31.50	32.00	33.35
800	49.90	34.00	52.61
900	52.90	36.60	57.34

Finally, a Pattern Search function minimization algorithm was used to find the optimal values of E_0 for fixed values of B ranging from 10^3 s^{-1} to 10^{15} s^{-1} . Parameter values estimated in this manner and Anthony's suggested values with both floating equilibrium and fixed equilibrium weight losses are shown in Tables 4.12, 4.13, and 4.14, along with the corresponding values of SSE.

Anthony's model predictions obtained using his original parameters are compared with the model predictions obtained using fitted parameters and floating V_f^* values for WK11 coal in Figure 4.10 and Table 4.16. Anthony's original model predictions appear to be lower than the experimental data at 800°C and higher than the experimental data at 600°C and 700°C . On the other hand, the fitted model predictions show good agreement with the experimental data at 800°C and 700°C , but are consistently lower than the experimental data at 600°C . However, significant improvements are seen relative to the original model predictions.

The fit of the model to the data is seen to be significantly better for the floating equilibrium yield than for the fixed equilibrium yield when Anthony's model parameters are used. Again, a major improvement is obtained by adjusting the parameters.

Table 4.12 Comparison of model parameters and SSE values (MRS)

Model	Isothermal Yes	No Fixed Variable	Equil. Yield Fixed	Parameters Fixed Fitted	Parameter Values	SSE
Single First-Order	X		X	X	$B_0 = 93.5 \text{ (l/sec)}$ $E_0 = 8.7 \text{ (kcal/mole)}$	413
		X	X	X	$B_0 = 7677 \text{ (l/sec)}$ $E_0 = 18 \text{ (kcal/mole)}$	242
Badzioch and Hawksley	X		X	X	$K_1 = 0.001031$ $K_2 = 589$ $Q = 1.8$ $A = 8.36 \times 10^4 \text{ (l/sec)}$ $B = 8.9 \text{ (kcal/mole)}$	2184
	X		X	X	$K_1 = 0.001031$ $K_2 = 589$ $Q = 1.8$ $A = 906 \text{ (l/sec)}$ $B = 6.37 \text{ (kcal/mole)}$	194
Kobayashi		X		X	$a_2 = 1.0$ $B_1 = 2 \times 10^5 \text{ (l/sec)}$ $B_2 = 1.3 \times 10^7 \text{ (l/sec)}$	270
			X	X	$E_1 = 25 \text{ (kcal/mole)}$ $E_2 = 40 \text{ (kcal/mole)}$	590
	X		X	X	$a_2 = 1.0$ $B_1 = 6030 \text{ (l/sec)}$ $E_1 = 18 \text{ (kcal/mole)}$ $B_2 = 6.6 \times 10^6 \text{ (l/sec)}$ $E_2 = 40 \text{ (kcal/mole)}$	230
Anthony		X	X	X	$K_0 = 1.0 \times 10^{10} \text{ (l/sec)}$ $V_f^* = 478$ $E_0 = 48.7 \text{ (kcal/mole)}$ $s = 9.36 \text{ (kcal/mole)}$	1079
	X		X	X	$K_0 = 1.0 \times 10^{13} \text{ (l/sec)}$ $E_0 = 48.7 \text{ (kcal/mole)}$ $s = 9.36 \text{ (kcal/mole)}$	588
	X		X	X	$K_0 = 1.0 \times 10^{13} \text{ (l/sec)}$ $E_0 = 18.9 \text{ (kcal/mole)}$ $s = 1.0 \times 10^{-3} \text{ (kcal/mole)}$	227

Table 4.13 Comparison of model parameters and SSE values (NB8)*

Model	Isothermal Yes	Equil. Yield No Fixed Variable	Parameters Fixed Fitted	Parameter Values	SSE
Single First-Order	X	X	X	$B_0 = 353$ (l/sec) $E_0 = 11.3$ (kcal/mole)	397
	X	X	X	$B_0 = 7853$ (l/sec) $E_0 = 18$ (kcal/mole)	154
Badzioch	X	X	X	$K_1 = 2.55 \times 10^{-3}$ $K_2 = 471$ $Q = 1.2$ $A = 8.36 \times 10^4$ (l/sec) $B = 8.9$ (kcal/mole)	11281
and Hawksley	X	X	X	$K_1 = 2.55 \times 10^{-3}$ $K_2 = 471$ $Q = 1.2$ $A = 4335$ (l/sec) $B = 84.$ (kcal/mole)	134
Kobayashi	X	X	X	$a_2 = 1.0$ $B_1 = 2.0 \times 10^5$ (l/sec) $E_1 = 25$ (kcal/mole)	722
		X	X	$B_2 = 1.3 \times 10^7$ (l/sec) $E_2 = 40$ (kcal/mole)	679
	X	X	X	$a_2 = 1.0$ $B_1 = 7530$ (l/sec) $E_1 = 18$ (kcal/mole) $B_2 = 1.44 \times 10^6$ (l/sec) $E_2 = 40$ (kcal/mole)	160
Anthony	X	X	X	$K_0 = 1.0 \times 10^{10}$ (l/sec) $V_f^* = 49\%$ $E_0 = 49.38$ (kcal/mole) $s = 9.36$ (kcal/mole)	1341
	X	X	X	$K_0 = 1.0 \times 10$ (l/sec) $E_0 = 48.7$ (kcal/mole) $s = 9.36$ (kcal/mole)	953
	X	X	X	$K_0 = 1.0 \times 10^{13}$ (l/sec) $E_0 = 18.9$ (kcal/mole) $s = 0.16$ (kcal/mole)	246

Table 4.14 Comparison of model parameters and SSE values (NB8)*

Model	Isothermal Yes	Equil. Yield No	Fixed Variable	Parameters Fixed Fitted	Parameter Values	SSE
Single First-Order	X		X	X	$B_0 = 6320$ (l/sec) $E_0 = 14.2$ (kcal/mole)	597
		X	X	X	$B_0 = 16035$ (l/sec) $E_0 = 19.12$ (kcal/mole)	439
Badzioch and Hawksley	X		X	X	$K_1 = 1.930 \times 10^{-3}$ $K_2 = 676$ $Q = 1.8$ $A = 6.1 \times 10^7$ (l/sec) $B = 16.3$ (kcal/mole)	1143
	X		X	X	$K_1 = 1.938 \times 10^{-3}$ $K_2 = 676$ $Q = 1.8$ $A = 6.1 \times 10^7$ (l/sec) $B = 16.3$ (kcal/mole)	513
Kobayashi		X		X	$a_2 = 1.0$ $B_1 = 2.0 \times 10^5$ (l/sec) $B_2 = 1.3 \times 10^7$ (l/sec)	7679
			X	X	$E_1 = 25$ (kcal/mole) $E_2 = 40$ (kcal/mole)	4681
	X		X	X	$a_2 = 1.0$ $B_1 = 4.8 \times 10^4$ (l/sec) $E_1 = 18$ (kcal/mole) $B_2 = 5.0 \times 10^6$ (l/sec) $E_2 = 40$ (kcal/mole)	394
Anthony		X	X	X	$K_0 = 1.0 \times 10^{13}$ (l/sec) $V_f^* = 48\%$ $E_0 = 54.8$ (kcal/mole) $s = 17.2$ (kcal/mole)	2842
	X		X	X	$K_0 = 1.67 \times 10^{13}$ (l/sec) $E_0 = 54.8$ (kcal/mole) $s = 17.2$ (kcal/mole)	670
			X	X	$E_0 = 55.2$ (kcal/mole) $s = 6.18$ (kcal/mole)	243

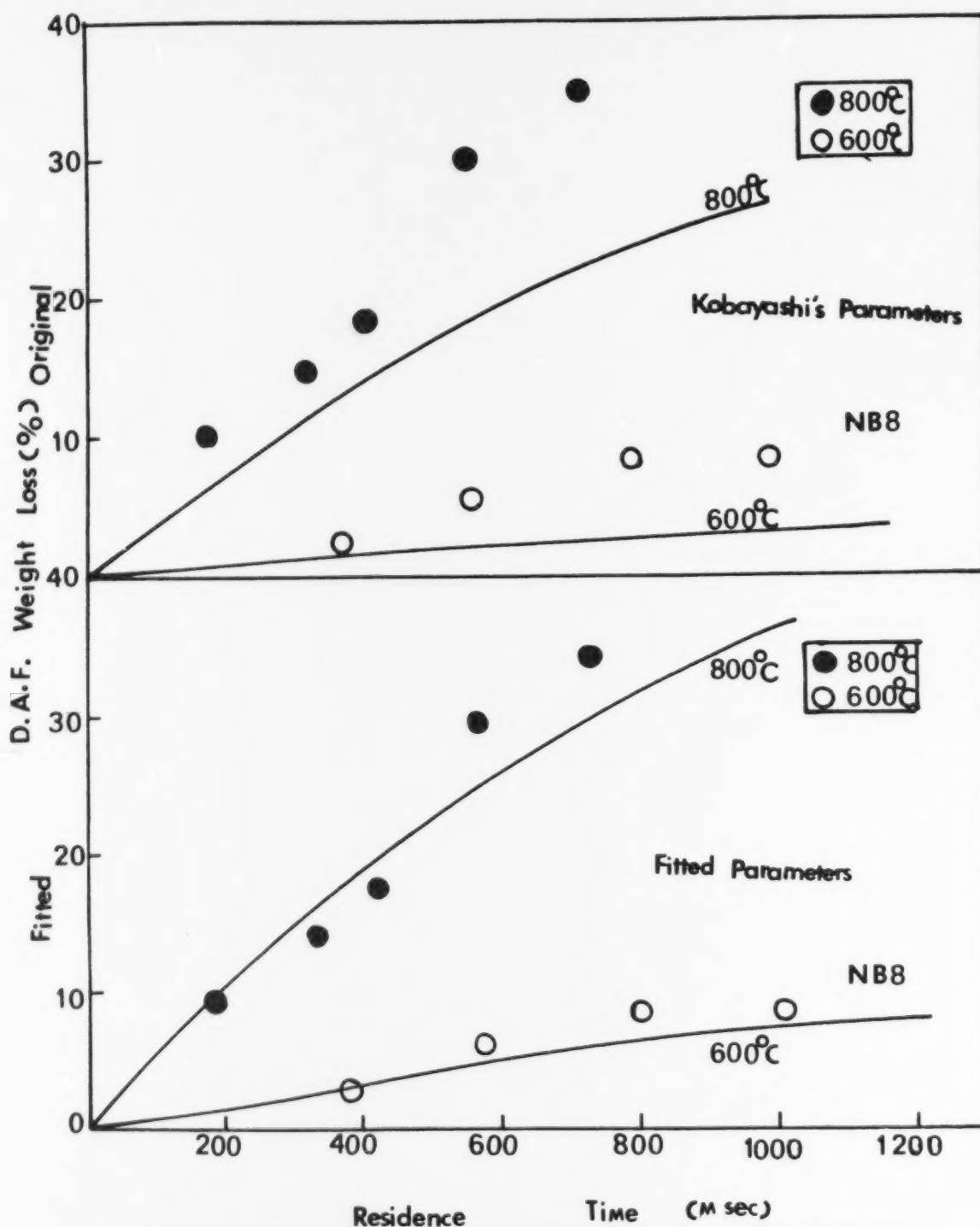


Figure 4.9 Comparison of Kobayashi's fitted model predictions with original model predictions (NB8)

Table 4.15 Comparison of Kobayashi's fitted model predictions
with original model predictions (NB8)

T(°C)	t _R (msec)	v*(exptl)	v*(original)	v*(fitted)
600	407.8	3.07	1.065	3.100
600	592.8	6.03	1.073	4.158
600	808.5	8.69	2.368	5.778
600	1019.0	9.22	3.015	7.257
800	210.4	9.21	6.608	8.365
800	352.9	14.47	12.461	16.278
800	434.0	18.33	15.214	19.750
800	578.9	29.79	19.263	24.895
800	735.0	34.87	22.600	29.219

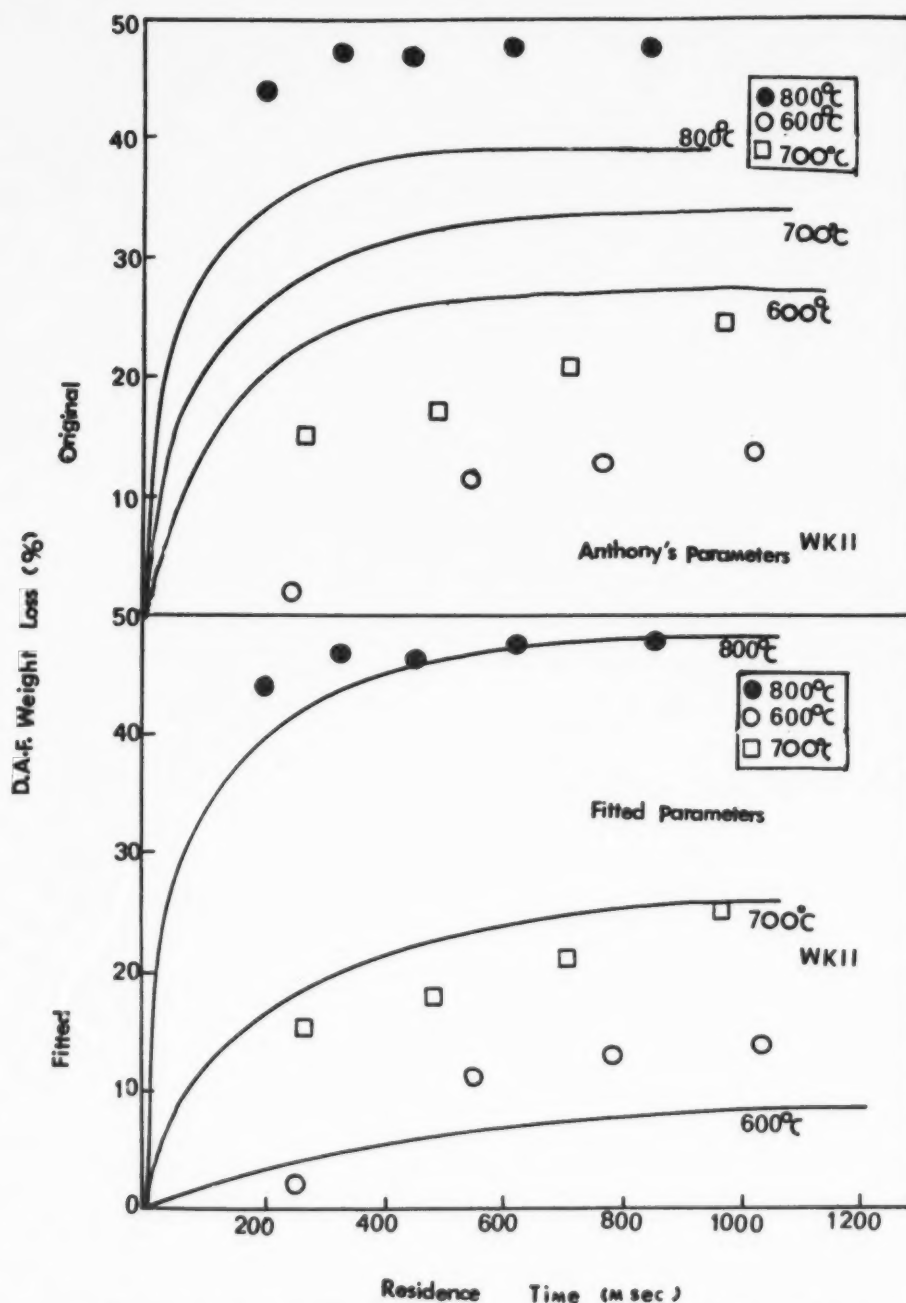


Figure 4.10 Comparison of Anthony's fitted model predictions with original model predictions (WKII)

Table 4.16 Comparison of Anthony's fitted model predictions with original model predictions (WK11)

T(°C)	t _R (msec)	V*(exptl)	V*(original)	V*(fitted)
600	244.9	2.590	21.486	4.474
600	557.2	12.090	22.345	6.194
600	779.2	13.790	22.830	7.200
600	1034.6	14.620	23.363	7.813
800	845.8	48.150	37.461	47.699
800	196.8	44.340	34.597	40.812
800	334.8	47.180	35.411	44.335
800	446.3	46.700	35.968	45.680
800	618.1	47.810	36.696	46.872
700	271.9	15.210	28.369	19.467
700	970.3	24.990	34.101	25.958
700	493.2	17.860	32.209	23.049
700	711.0	20.850	33.543	24.790

Discussion

Comparative listings of the model parameters (with both original and fitted parameters) and the sum of squares of error values for all five models and all three coals are given in Tables 4.12, 4.13, and 4.14. As indicated by the smaller values of SSE, the fitted isothermal models (single first-order reaction model and Badzioch-Hawksley model) provide reasonable correlations of the experimental data. However, the arbitrary specification of an isothermal reaction time limits the flexibility required to describe nonisothermal pyrolysis in any reactor, and leads to anomalously low activation energies. Therefore, these two models are eliminated from further consideration.

Results obtained for the parameters determined by fitting Anthony's model to our data are compared with results based on Anthony's original model parameters in Tables 4.12, 4.13, and 4.14. The fitted parameters for the medium-swelling high rank coal (WK11) are close to Anthony's values, although the spread of the fitted activation energy distribution is narrower than Anthony's. On the other hand, in contradiction to Anthony's prediction, the fitted parameters for NB8 and MRS coals suggest that a single reaction with a low activation energy dominates the decomposition of low swelling, low rank coals. However, this result does not eliminate the possibility that the pyrolysis may be better described as a finite set of decomposition reactions with different activation energies.

Kobayashi's model has this form. However, for this model as well, the values of the fitted parameters for all three coals imply that a low activation energy first-order reaction dominates the overall pyrolysis over the temperature range 400°C-900°C. This can be shown by comparing values of K_1 and K_2 at 900°C. As shown in Table 4.17, K_1 is much larger than K_2 for all three coals. Thus, adding a second reaction with a high activation energy makes little difference for a medium swelling high rank coal like WK11 and essentially no difference for low swelling low rank coals like MRS and NB8.

The conclusion is that at temperatures below 1000°C pyrolysis of MRS and NB8 coals and presumably of other low swelling low rank coals is well described by a single first-order decomposition rate law; replacing this law by a discrete set of reactions with higher activation energies does not improve the fit significantly and replacing it with a continuous distribution of high activation energies makes the fit worse. This conclusion basically supports the findings of Kobayashi and is inconsistent with those of Anthony and Suuberg. On the other hand, Anthony's model is quite consistent with our results for the pyrolysis of a medium swelling high rank coal. We are aware of the fact that the evidence obtained by Suuberg et al. (1978) on coal pyrolysis product distributions supports the notion that devolatilization is governed by a set of reactions with varying activation energies. We are currently modifying our laminar flow reactor to permit measurement of gas product compositions, and so to determine whether this too is a reflection of the

difference between the heated grid and the laminar flow reactor types. For now, the contradiction must remain unresolved.

CONCLUSIONS

The preceding results show that wide discrepancies may occur between measured values and predicted values of both asymptotic and transient weight losses when either Kobayashi's or Anthony's models are used with their originally proposed parameters. Table 4.11 shows the substantial errors in asymptotic weight loss predictions that result from using Kobayashi's model with a fixed value of a_1 . The weight loss in this case is overestimated at low temperatures and underestimated at high temperatures. On the other hand, Anthony's model with a temperature-independent value of V_f consistently overpredicts the asymptotic weight loss. Representative discrepancies in the transient weight loss predictions are shown in Figures 4.9 and 4.10 and are also seen to be substantial. The conclusion here is that the generality of neither model is as great as might have been inferred from the original model presentations.

Both models can be improved by explicitly building in temperature-dependent asymptotic weight losses. This is straightforward with Anthony's model which has V_f as a parameter. With Kobayashi's model, an approximate method is to set a_1 equal to the expected value of $V_f(T)$; a more precise but more cumbersome method would be to adjust the value of a_1 and a_2 simultaneously.

Kobayashi's model with its original parameters does a good job of representing the transient weight loss data for Montana Rosebud sub-bituminous coal, but is somewhat less successful with North Barber No. 8 subbituminous, and fails completely for Western Kentucky No. 11 bituminous. Anthony's model with its original parameters is relatively poor for all three coals, but is somewhat better than Kobayashi's for the bituminous coal.

Regression studies show that several models can be used to fit most of the weight loss data with more or less equivalent degrees of success; in fact, a model consisting of a single first-order decomposition reaction is as good as any of the more complex models for the two low rank coals studied and not two much worse than the best of the models for the bituminous coal. Moreover, the single reaction model parameter values for both low rank coals are quite similar: the preexponential factor is roughly $7750(s^{-1})$, and the corresponding activation energy is 18 kcal/mole. All fitting studies support the notion that the kinetics of low rank coal pyrolysis are dominated by a single first-order reaction with a low activation energy. This contradicts the findings of Anthony (1976) and Suuberg (1978), whose results support the conclusion that pyrolysis is in reality a series of parallel reactions with activation energies distributed over a much higher range. On the other hand, the data obtained in this study for the bituminous coal are quite consistent

with Anthony's picture, albeit the spread of the activation energy distribution is narrower than that proposed by Anthony.

In summary, we draw the following conclusions.

1. Kobayashi's model with its original parameters does a reasonable job of representing the pyrolysis of the two low rank coals studied. Improvements can be made by adjusting the parameter values, but not to the extent that the original values are discredited. Anthony's model appears to be superior for describing the pyrolysis of high rank coals.
2. Anthony's model with its original parameters fails to fit the data for any of the coals studied. Considerable improvements are obtained for bituminous coal by allowing the asymptotic weight loss to vary with temperature, and decreasing the standard deviation of the activation energy distribution. However, for low rank coals the model is consistently outperformed by a single first-order decomposition reaction model with a low activation energy.
3. The contradiction between the results obtained here for low rank coals and those of Anthony (1976) and Suuberg (1978) as yet admit of no resolution, although they may be attributable to the difference between the operating characteristics of laminar flow reactors (such as those used in this study and by Kobayashi) and of electrically heated grid reactors (such as those used by Anthony and Suuberg).

Table 4.17 Comparison of K_1 and K_2 for all three coals

Coal	$K_1(s^{-1})$	$K_2(s^{-1})$
MRS	2.66	0.23
NB8	3.33	0.05
WK11	21.20	0.17

SECTION 5

ELEMENTAL RELEASE

Among the potentially hazardous trace and minor elements in coals, sulfur is present in the greatest amount, and mercury, arsenic, and lead are perhaps the most volatile (Agreda, 1979). These elements were therefore selected as the subjects of this study.

CHEMICAL ANALYSES

Proximate, ultimate, and trace/minor element analyses were carried out on the coals and chars and produced in this study. Every effort was made to ensure the accuracy and precision of the analyses and to eliminate any bias in the data due to instrument drift or analysis bias. Certified standards were run concurrently with the samples for almost every analyte. If the analysis of the standard did not agree with the certified value, the entire lot of analyses was discarded and new analyses made.

Moisture in the coal and char samples was determined by establishing the loss in weight of 1.0 g of sample heated to 104-110°C for 1 hour in a moisture oven with bone dry air circulation. ASTM-D-3173 method was followed.

The ash content was determined by weighing the residue remaining after burning 1.0 g of coal at 950°C in a muffle furnace. The same sample for moisture analysis was used. ASTM-D-3174 was followed.

Sulfur analyses were carried out with a Fisher-Sulfur Analyzer Model 470. The analyzer combusts the sulfur in the samples and detects the sulfur dioxide produced through. This analyzer is extremely accurate and precise in the analysis of sulfur in coal and coke. However, the analyzer does not detect sulfate sulfur which occurs in small quantities in most coals. Certified coal standards were used to calibrate the analyzer and to check its accuracy periodically.

As, Hg, and Pb analyses were carried out using a Perkin Elmer 603 Atomic Absorption Spectrophotometer, and HGA-2200 graphite furnace, and a cold vapor mercury analysis system. Ramp heating was used for the drying and charring steps, and normal, temperature controlled, or time controlled heating was used during atomization, depending on the volatility of the element. NBS certified standards were run concurrently to ensure the accuracy of the analysis.

RESULTS

The weight loss data obtained in Section 4.1 were used in the following equations to calculate the fractional retention of elements in chars:

$$F_H = X_H (1 - V) \quad (5.1)$$

where

F_H = g element in char/g feed coal

X_H = g element in char/ g char

V = fractional weight loss

$$G_H = F_H / X_C, \left(\frac{\text{g element in char}}{\text{g element in feed coal}} \right) \quad (5.2)$$

where

X_C = g element in feed coal/g feed coal.

The fractional loss of the element can be obtained as

$$Z = 1 - F_H = \frac{(X_C - G_H)}{X_C}; \left(\frac{\text{g element lost}}{\text{g element in feed coal}} \right) \quad (5.3)$$

These equations are valid for all three bases (a.r., m.f., and d.a.f.), as long as all parameters are expressed on the same basis. Values of F_H , G_H , and Z were calculated using both corrected and uncorrected weight loss values in Equations 5.1, 5.2, and 5.3. To distinguish values determined using the corrected V^* values from those determined using the uncorrected values, the latter are subscripted with an "A" instead of "H" (for example: G_A vs. G_H).

Figures 5.1, 5.2, 5.3, and 5.4 show the fractional retention of the elements as functions of residence time and temperature. The solid lines in Figures 5.1 and 5.2 are model predictions to be discussed later. The trends are clear for the four elements except in the case of mercury in NB8 coal. Inspection of these figures clearly shows that the kinetics of elemental release differ considerably from the low-swelling subbituminous coal to the medium-swelling bituminous coal, with the release in the latter coal being more rapid and proceeding to a greater extent. This is not unexpected since the devolatilization rates and perhaps the mechanisms are quite different. The devolatilization of high or medium-swelling coals (caking coals) is often accompanied by the deformation of the coal structure and the formation of a highly porous char containing entrapped bubbles. It is likely that trace and minor elements leave the char particles in significant quantities during the deformation and resolidification of the char particles. The element

retentions greater than 100% observed in Figure 5.2 are physically impossible and suggest that errors in the weight loss estimates still remain after the corrections discussed in Sections 3 and 4 have been applied.

As a first step toward the modeling of elemental release, the retention and loss values for all four elements were linearly regressed with time and temperature. The null hypotheses that the slopes with respect to time and temperature equal zero were tested at levels of significance of 20%, 10%, and 2% using a two-tailed t-test. The detailed results are given by Kau (1980), and the outcomes of the significance tests are summarized in Tables 5.1 and 5.2. Inferences about element volatilities can be drawn from these results, in accordance with the following guidelines outlined by Agreda (1979).

- o If $X_H =$ versus T has a slope significantly greater than zero, indicating that the char is becoming progressively enriched in the element as the temperature increases, and $G_H =$ versus T also has a slope equal to or greater than zero (the latter due to underestimation of V^*), indicating that the absolute amount of element in the char is remaining constant, it may be inferred that the element is not significantly released from the particle in the temperature range investigated.
- o If the slope of $X_H =$ versus T is greater than zero, and that of $G_H =$ versus T is less than zero, the elemental release from the coal is significant, but its fractional release at a given temperature is less than that of the total volatile matter.
- o If the slope of the $X_H =$ versus T curve is equal to zero, and that of $G_H =$ versus T is less than zero, the elemental release is proportional to the total volatile matter release.
- o If the slopes of $X_H =$ and $G_H =$ versus T are less than zero, the elemental release is proportionally greater than the total volatile matter release.

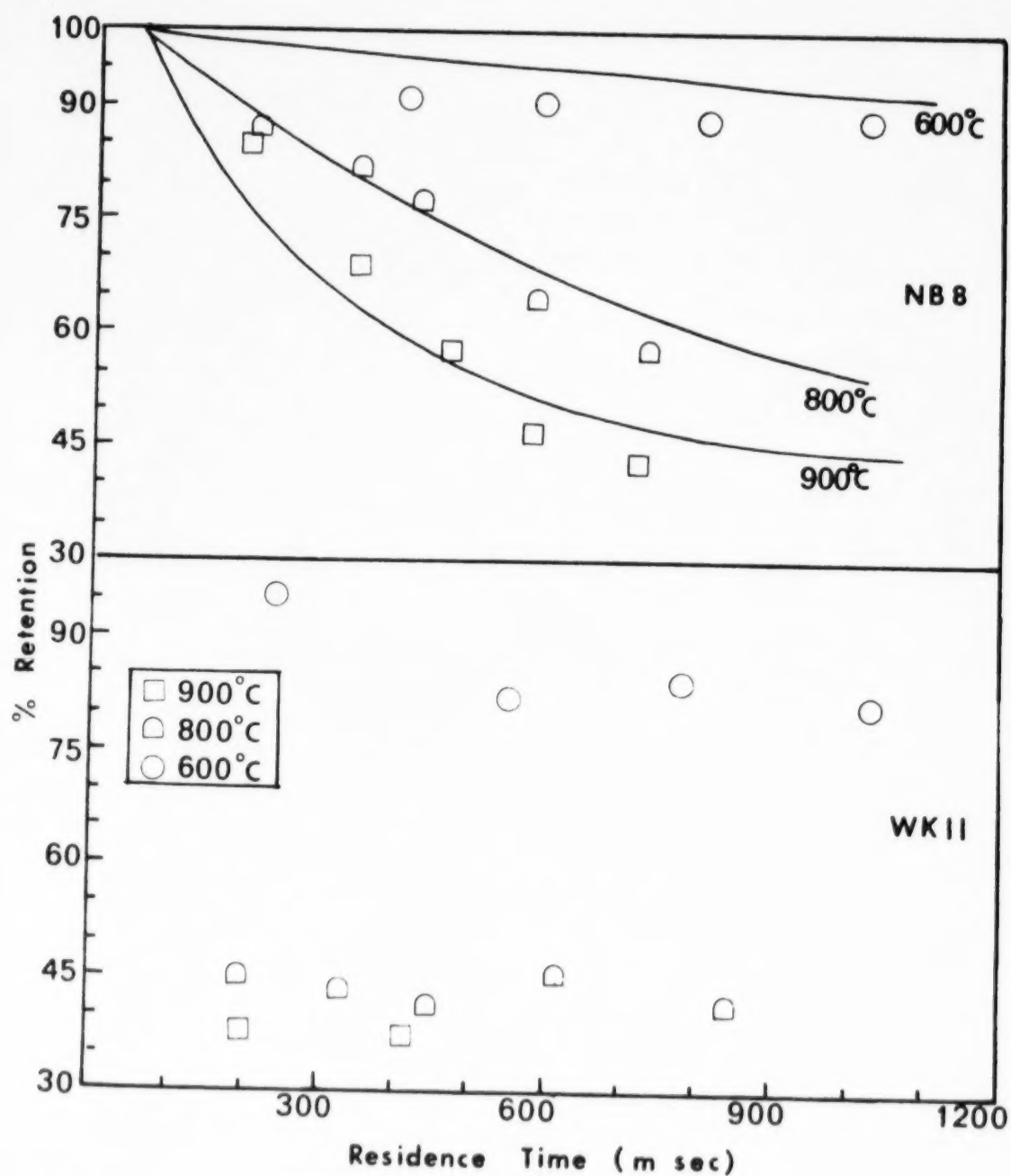


Figure 5.1 Sulfur retention in LFR chars

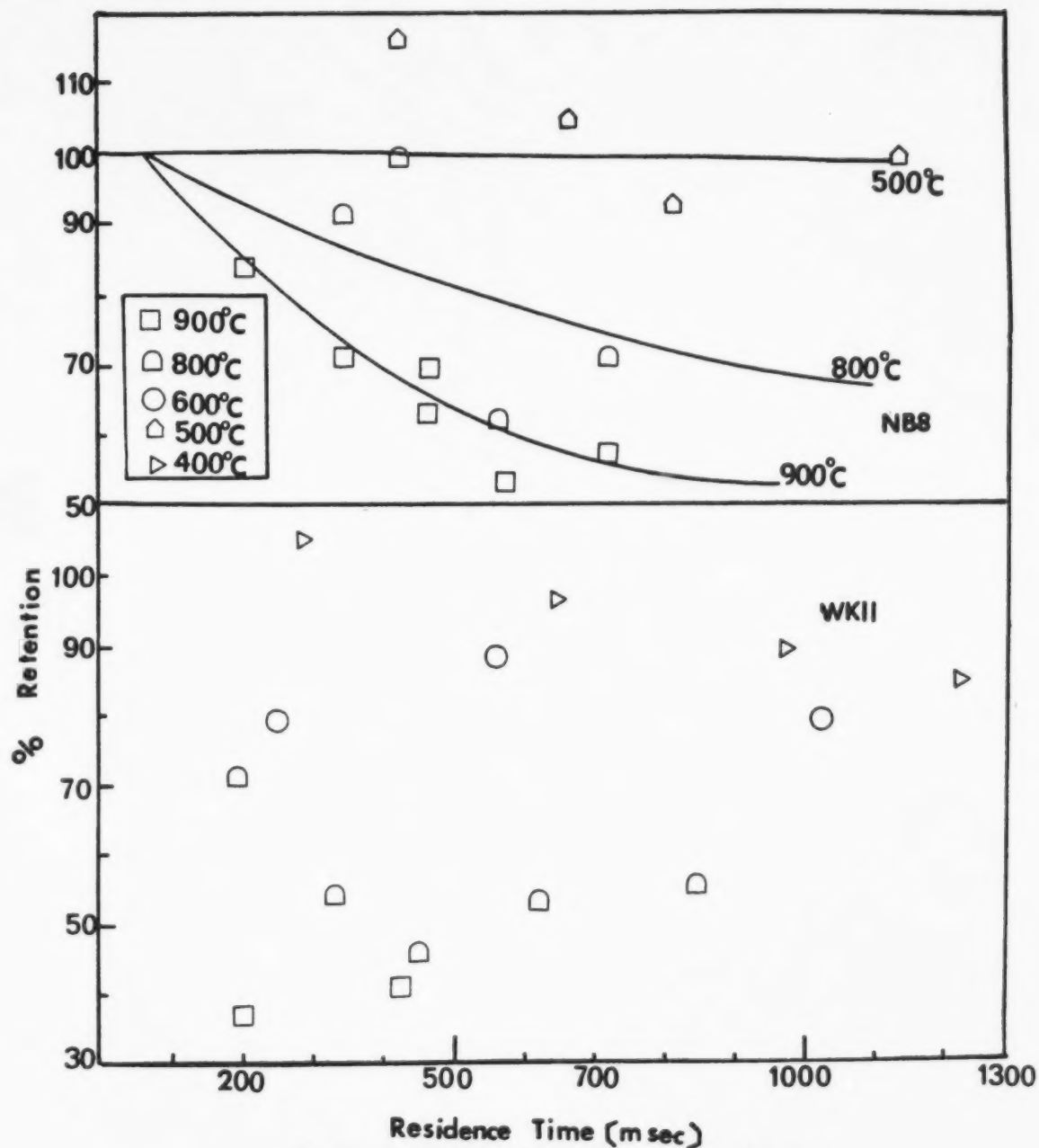
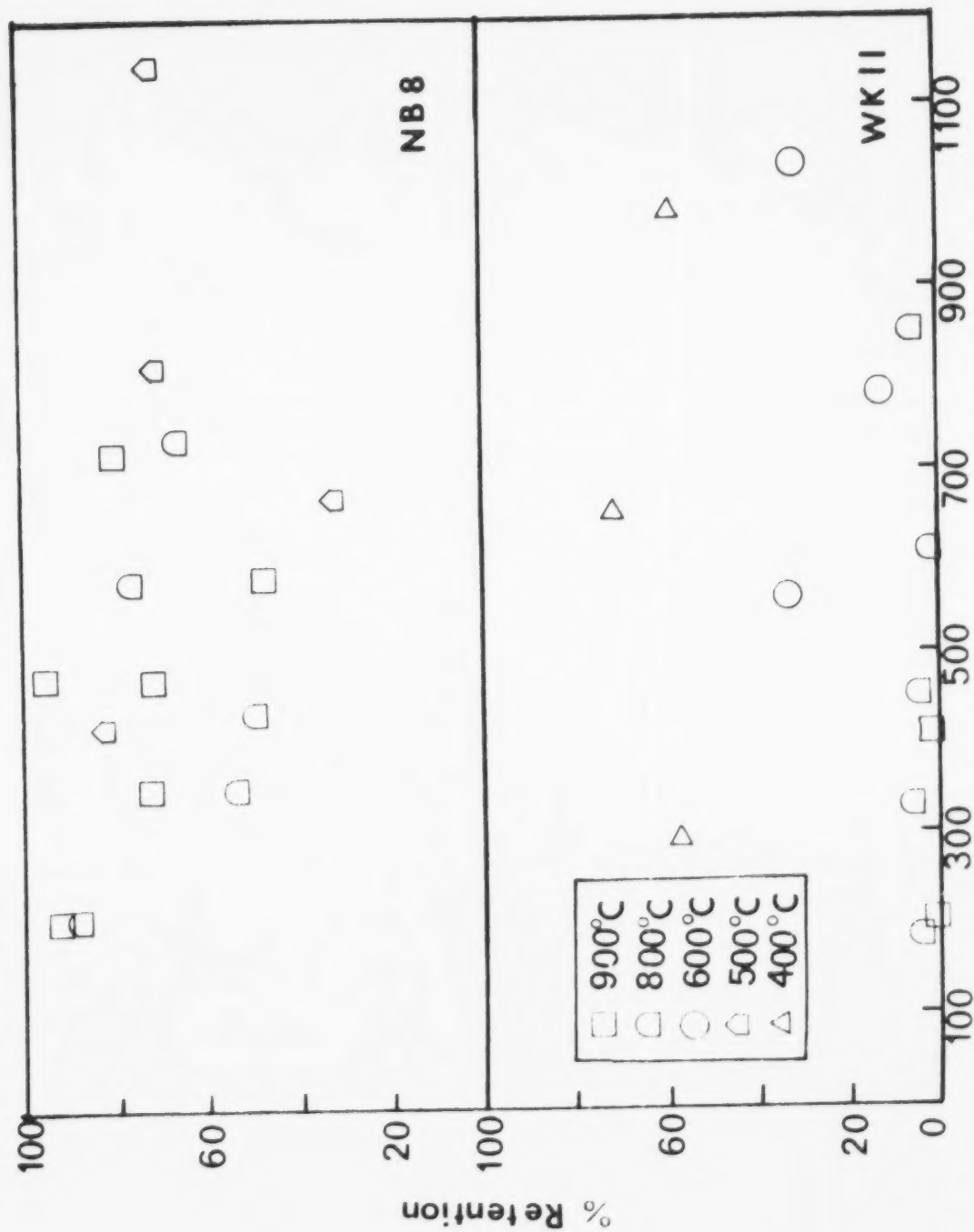


Figure 5.2 Lead retention in LFR chars



Residence Time (m sec)
Figure 5.3 Mercury retention in LFR chares

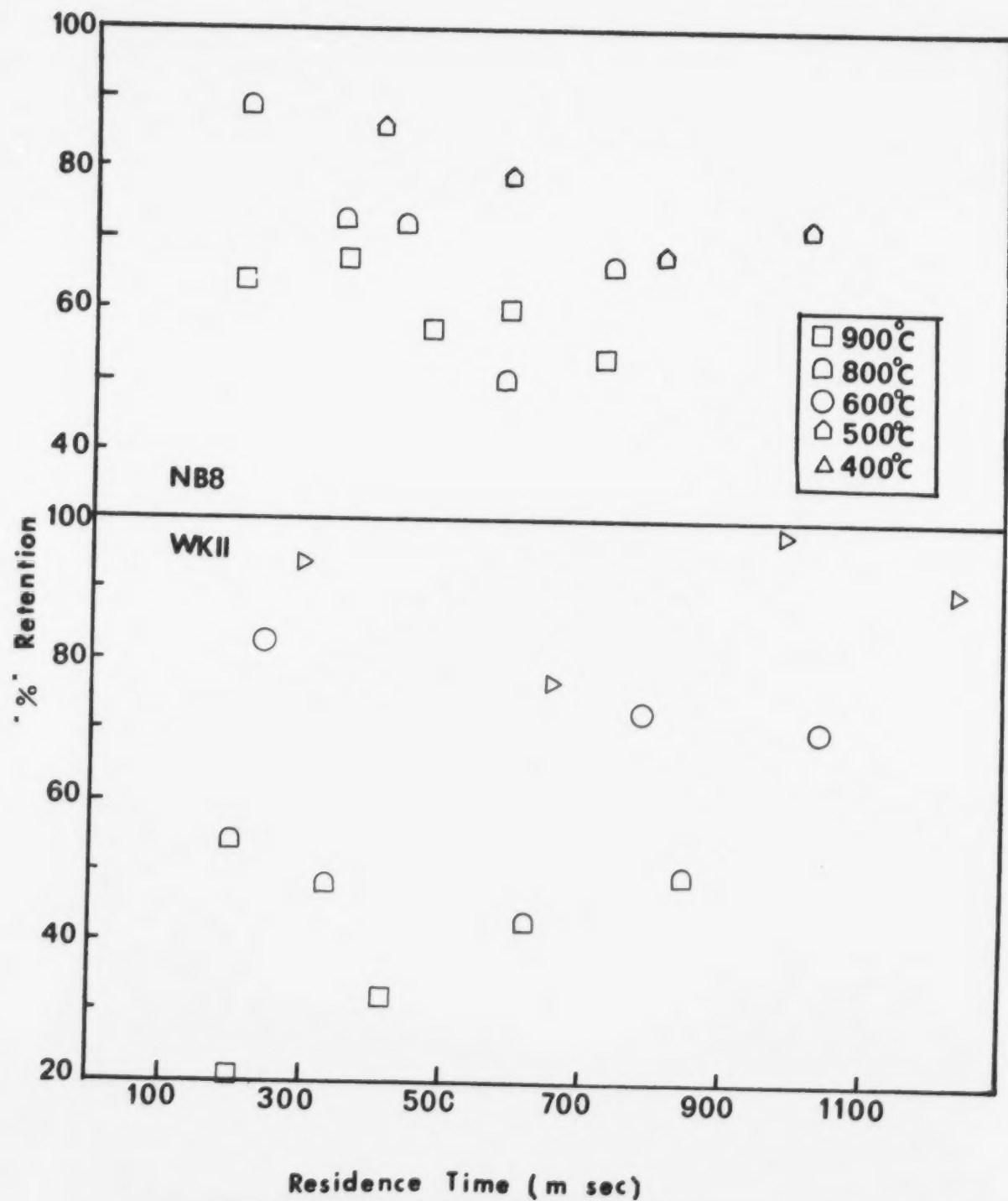


Figure 5.4 Arsenic retention in LFR chares

Table 3.1 Significant correlations in WK11 chars

WK11 Coal	Element-Temperature Correlations					Element-Time Correlations				
Element	$X_H^=$	$G_A^=$	$G_H^=$	F_A	F_H	$X_H^=$	$G_{A_D}^=$	G_H	F_A	F_H
S	**	**	**	**	**	+ o	+ o	+ o	+ o	+ o
Hg	**	**	**	**	**	- o	- o	- *	- o	- *
Pb		*	**	-	**					x
As	*	**	**	**	**					x

o = significant at 20% level
 * = significant at 20% level
 ** = significant at 2% level

x = undetected trend
 - = negatively correlated
 + = positively correlated

Table 5.2 Significant correlations in NB8 chars

NB8 Coal	Element-Temperature Correlations					Element-Time Correlations				
Element	X_H	G_A	G_H	F_A	F_H	X_H	G_A	G_H	F_A	F_H
S	**	**	**	**	**					x
Hg	+ *	+ o		+ o	x	<u>o</u>	-	-	-	-
Pb			<u>o</u>		<u>o</u>					x
As		-	**	-	**			<u>o</u>		<u>o</u>

o = significant at 20% level
 * = significant at 10% level
 ** = significant at 2% level

x = undetected trend
 - = negatively correlated
 + = positively correlated

- o If the slope of F_H versus T is equal to zero (indicating that no appreciable amounts of the element have been released), the element is not volatile. If it is less than zero, the element is released to an extent that increases with increasing temperature. The behavior of F_H simply mirrors that of $F_H^=$, but more importantly, it allows easy visual examination of the data. Since F_H must range from 1.0 (complete retention) to 0.0 (no retention), its value quickly indicates whether the element is retained in the char or not. This is useful because the linear regression analyses only detect consistent trends. If a retention (F_H) drops at low temperatures and then remains at a constant value, no linear trend would be found; nevertheless, it would be obvious that the element had been released from the coal.
- o If the slopes of $X_H^=$ and $G_A^=$ versus T are positive and the slope of $G_H^=$ versus T is negative, the element is released to a lesser extent (as a function of T) than the ash.
- o If the slope of $X_H^=$ versus T is positive and that of $G_A^=$ versus T is negative, the element is released to an extent large enough to overcome the ash loss effect.
- o The interpretations of the slopes of $X_H^=$, $G_H^=$, and F_H versus t_R are similar to those versus T . The rates of elemental release are compared with V versus t_R instead of V versus T , however.
- o If no slopes are found to be significantly different from zero for a given element, either the scatter in the data is too large for any significant trends to be detected, or the trends cannot be detected through linear regression.

From interpretation of the information presented in Tables 5.1 and 5.2 the conclusions are summarized as follows:

1. The emissions of As and Pb in NB8 coal and Pb in WK11 coal are proportional to the total volatile matter release over the temperature range of 400°C-900°C.
2. The emissions of S, Hg, and As in WK11 coal and S in NB8 coal are proportionally greater than the total volatile matter release over the temperature range of 400°C-900°C.
3. The emissions of all four elements in both coals increase as temperature increases from 400°C to 900°C except in the case of Hg in NB8 coal, for which the scatter was too great for a trend to be observed.

4. The elemental release of Hg in NB8 coal and As and Hg in WK11 coal increase as the residence time increases from 170 milliseconds to 1200 milliseconds. The results indicate that temperature appears to be more important than residence time in determining the extent of elemental release during pyrolysis of the coals studied over temperatures from 400°C to 900°C and residence times from 170 msec to 1200 msec.

Agreda (1979) studied the emissions of these four elements using NB8 coal in the same LFR system and using both NB8 and WK11 coal in a batch system. The retentions of elements in the chars obtained in his study are shown with the results from this study in Figures 5.5, 5.6, 5.7 and 5.8. It is evident that results from the present study show higher elemental release than those from Agreda's LFR study. This may be due to the effect of the hot-water cooling system, which was successfully used in this study to minimize tar recondensation and thus, presumably, element recondensation.

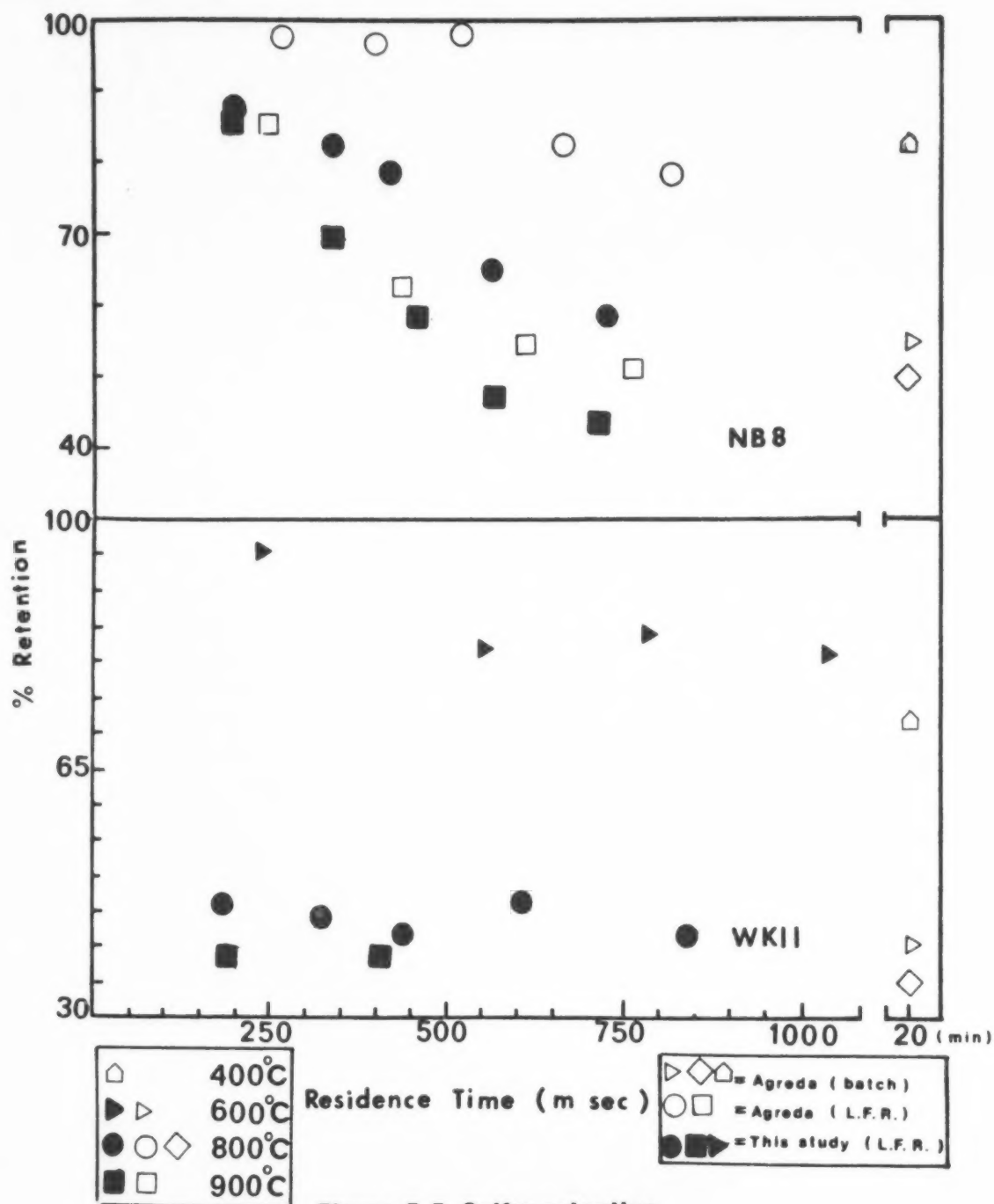


Figure 5.5 Sulfur retention

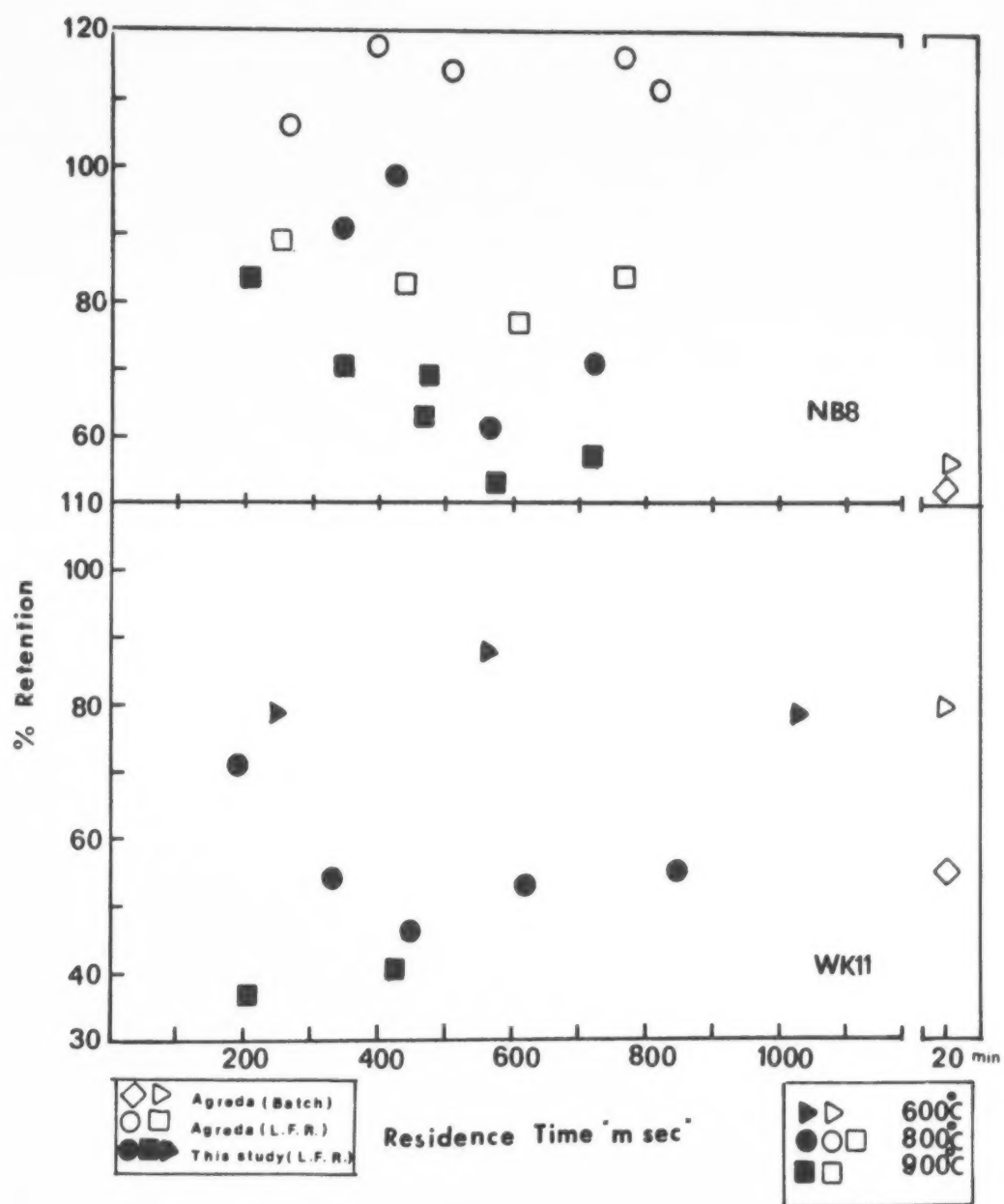


Figure 5.6 Lead retention

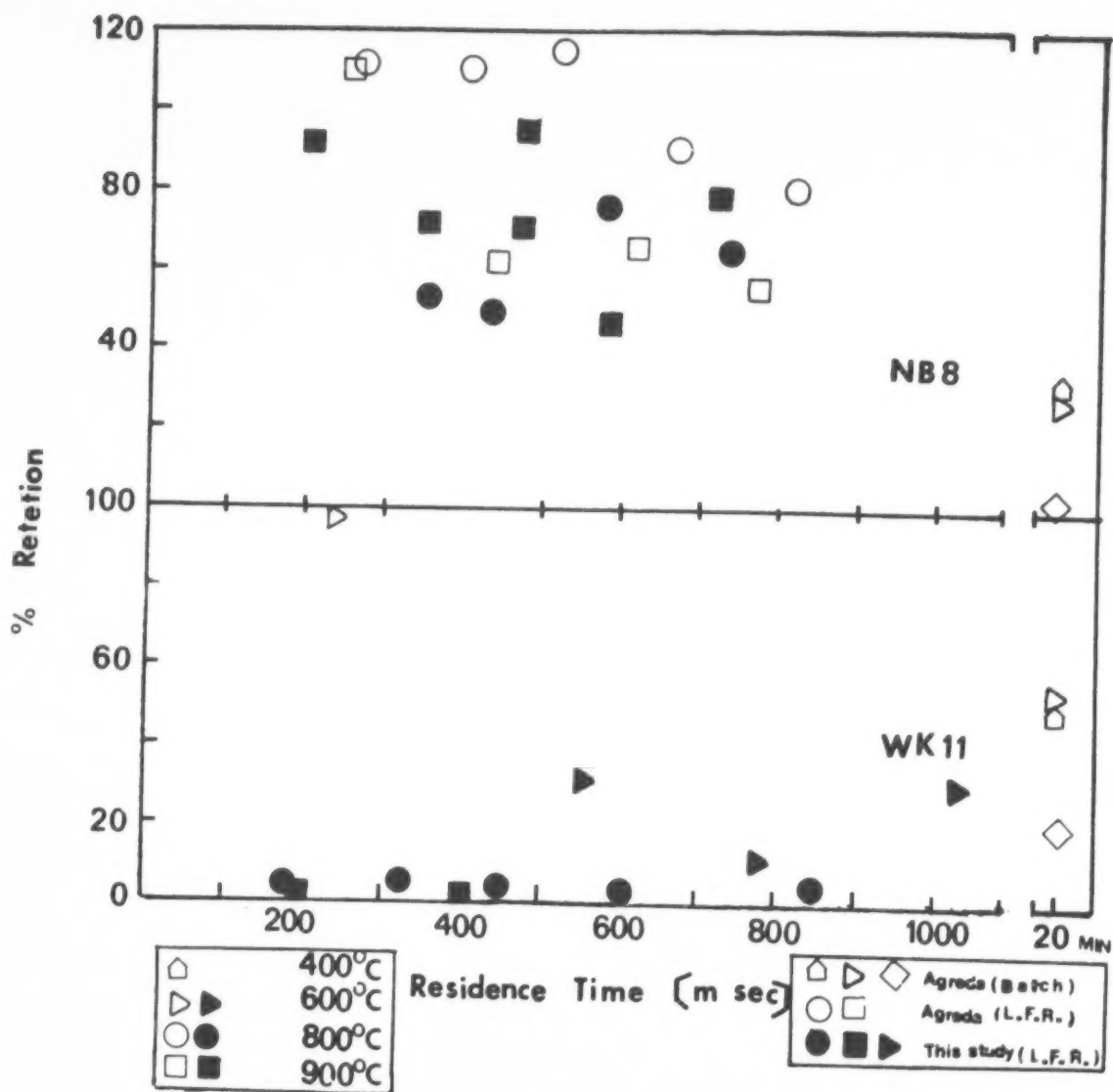


Figure 5.7 Mercury retention

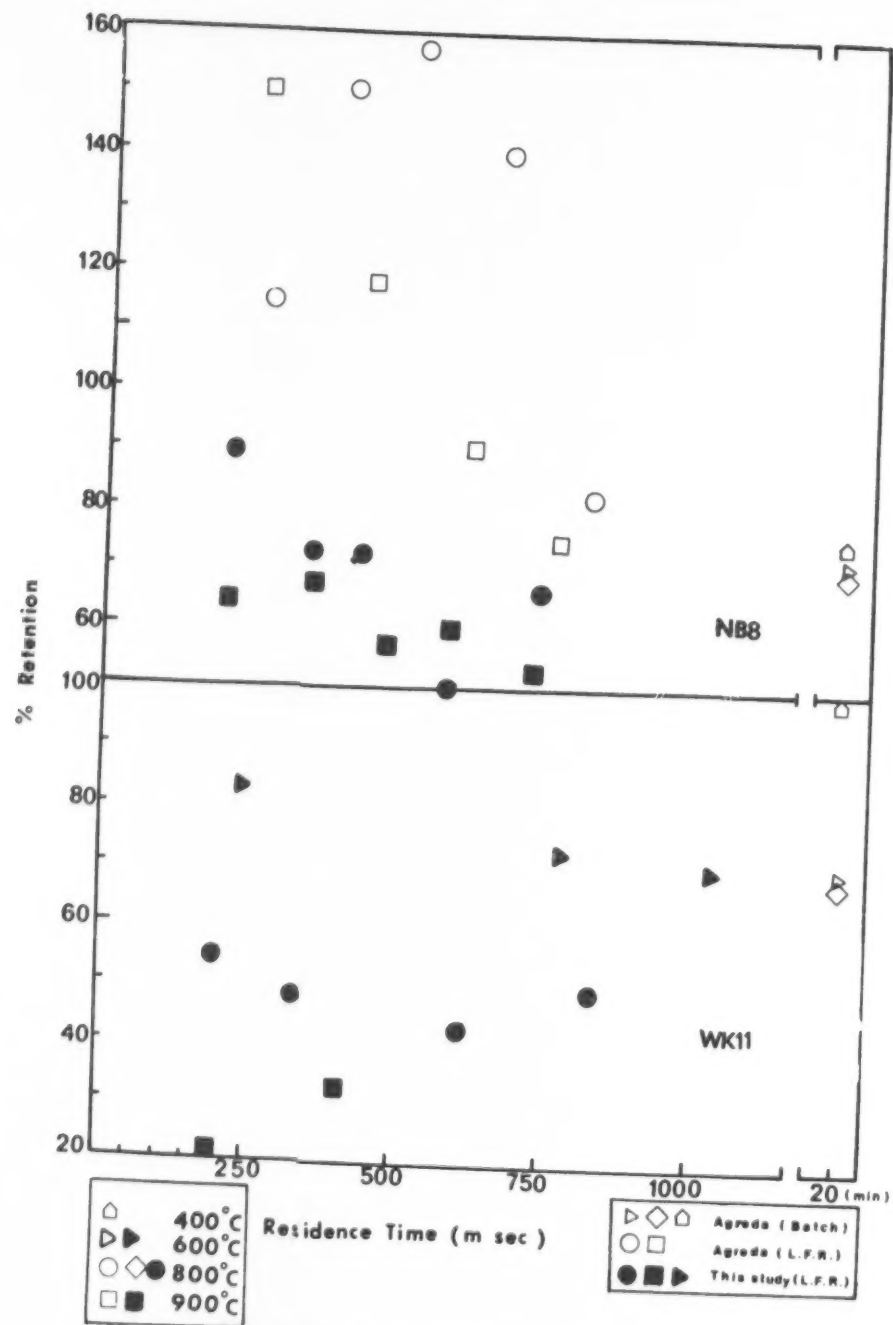


Figure 5.8 Arsenic retention

MODELING

Despite the scatter in the data and the uncertainties in the sampling, analysis and calculation of process parameters, efforts have been made to model elemental release in coals during fast pyrolysis. As discussed in Section 1.7, Agreda (1979) proposed a first-order release model coupled with equilibrium release parameters determined in batch pyrolysis studies to correlate the results from LFR experiments. Agreda's expression for the fractional release of an element is:

$$v^* = \frac{\int_0^t R \, dt \, K(v_f^*) \exp\left(\int_0^t K \, dt\right)}{\exp\left(\int_0^t R \, K \, dt\right)} \quad (5.4)$$

$$K = B e^{-E/RT}$$

where

Z_f = equilibrium fractional release at each temperature.

The values of Z_f calculated from the following equation were used in Equation 5.4 to obtain Z :

$$\text{where } Z_f = H(T - T_C) \{ Z_{fe} [1 - e^{-b(T - T_C)}] \} \quad (5.5)$$

Z_{fe} = high temperature limit of V_{ef} ,

T_C = critical temperature at which elemental release begins,

b = constant, and

$H(T - T_C)$ = unit step function.

Values of Z_f , T_C , and b for different coals obtained in Agreda's (1979) study are given in Table 1.4. Particle residence times and time-temperature histories are calculated as indicated in Section 3.

The isothermal form of Equation 5.4 is

$$Z = Z_f (1 - e^{-Kt}) \quad (5.6)$$

This equation can be used for roughly estimating the model parameters. Linear regression of t versus $\ln [1 - Z/Z_f]$ yields $(-K)$ as the slope, and linear regression of $\ln(K)$ versus $1/T$ yields $\ln(B)$ as the intercept and $-E/R$ as the slope. Values of the model parameters for S and Pb in NB8 coal obtained in this manner are given in Table 5.3. No parameters were obtained in the other cases of NB8 coal and in all four cases of WK11 coal because of the high degree of scatter of the data.

The solid lines shown in Figures 5.1 and 5.2 are the predictions of this model. Integration of Equation 5.4 was carried out using Simpson's rule. It is clear that the elemental release parameters obtained for a low-swelling coal (NB8) cannot be used to model the elemental release in a medium-swelling coal (WK11).

Table 5.3 Elemental release model parameters (NB8)

Element	Parameter	
	E	B
S	19100 cal/mol	13300/s ⁻¹
Pb	17100 cal/mol	2800/s ⁻¹

In the absence of good kinetic parameters for the first-order elemental release model, a simple linear model was used as a rule of thumb predictor of the rates of elemental release (Agreda, 1979)

$$Z = 0 \quad T < T_C \quad (5.7)$$

$$= \min \{kV^*, Z_f(T)\}, \quad T > T_C$$

where k = an adjustable proportionality constant. This model presumes that an element is not released until the temperature reaches a threshold value, T_C , and then is released at a rate proportional to the rate of d.a.f. weight loss. The proportionality constants and correlation coefficients estimated from linear regression are listed in Table 5.4. The model provides rough estimates of the elemental release for those cases having significant correlations.

The proportionality constants K for sulfur in both coals are roughly equal to 1.0 and the correlations are extremely good ($r = 1.0$). These results are consistent with Agreda's (1979) results. Figure 5.9 shows the

correlations between fractional sulfur release and d.a.f. weight losses for both coals. High values of the correlation coefficient indicate the total amount of sulfur released is proportional to the amount of d.a.f. volatile matter released. The reason for such behavior is not clear since sulfur exists in at least three primary forms in coal (pyrites, sulfates, and organically bound sulfur). A possible explanation could be inferred from the findings of Kuhn et. al. (1977) who report that at temperatures higher than 450°C sulfur is released at much higher rates from the organic portion of coal than from the inorganic portion of coal. This conclusion (sulfur release is proportional to the d.a.f. volatile matter released) seems to contradict the conclusion that sulfur release is proportionally greater than the total volatile matter released obtained in the previous section. However, in view of the over-simplified linear regression method used in that section, the conclusion obtained in this section should be more reliable.

Table 5.4 Significant d.a.f. weight loss-element correlations

Coal		WK11		NB8		
Element	Slope	r^2	T_C (°C)	Slope	r^2	T_C (°C)
Analyte	(Ks)			(Ks)		
S	1.1830	0.9965	223	1.1300	0.9895	223
Hg	1.2606	0.6651	110	-0.4877	0.0850	110
Pb	1.0339	0.5480	499	1.3330	0.2133	499
As	1.0527	0.7749	223	0.5891	0.4924	223

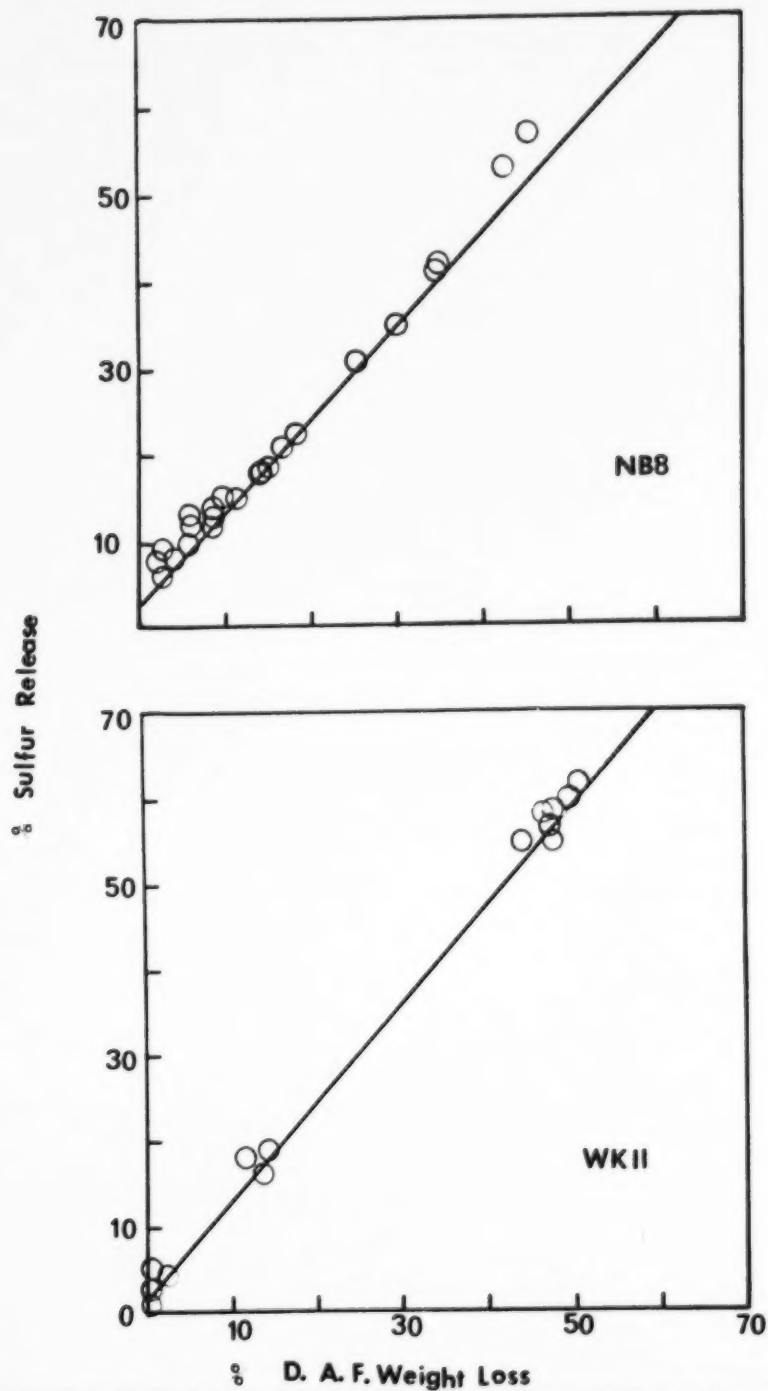


Figure 5.9 Fractional sulfur release at different d.a.f. weight losses

CONCLUSION

Sulfur, mercury, lead and arsenic are released in significant quantities during fast pyrolysis, with the release being complete in tenths of seconds. The release of these elements from low-swelling coal is quite different from that in medium-swelling coal, with elements being released much more rapidly and to greater extents from the latter. The emissions of arsenic and lead in NB8 coal and lead in WK11 coal are proportional to the total volatile matter release and the emissions of mercury and arsenic in WK11 coal are proportionally greater than the total volatile matter release. The amount of sulfur release was nearly directly proportional to the amount of dry-ash-free volatile matter released for NB8 and WK11 coals. This confirms the findings of Agreda (1979).

The kinetics of sulfur and lead release from NB8 coal have been modeled using a first-order reaction model coupled with a model for equilibrium release derived from batch pyrolysis experiments (Agreda, 1979). The lack of precision in the retentions of other volatile trace elements prevented the meaningful determination of kinetic parameters for the release of these elements.

NOMENCLATURE

A	fractional ash content of coal or char
a	constant in (1.3)
a_1, a_2	constants in (1.4)
B, B_1, B_2	pre-exponential factors in Arrhenius law
b	constant
C	heat capacity
c^p	constant in (1.3)
d	constant in (4.9)
D	particle diameter
E, E_1, E_2	activation energies
E_o	mean activation energy for a distribution
E_C, E_H	ash fractions of particles collected from cold and hot runs
F_H	mass of element in spent char/mass of coal fed
G_H	mass of element in spent char/mass of element in feed coal
K	devolatilization rate constant
K_s	constant in (1.25)
k_1, k_2	constants in (1.3)
M	fractional moisture content
N	quantity defined by (3.8)
N_H	quantity defined by (4.4)
Q	constant in (1.3)
R	gas constant
R_1, R_2	char yields
R_H	total mass of recovered char/mass of coal fed
r_C, r_H	tracer mass fractions in feed coal and char, respectively
SSE	sum of squares of residuals
s	standard deviation of Gaussian activation energy distribution
T	temperature
T_C	critical temperature above which release occurs
t	time
t_H	heating time constant
t_I	equivalent isothermal residence time
t_R	residence time
V, V_1, V_2	fractional weight losses (volatile yields)
V_f	long-time asymptotic value of V
V_{fe}	high temperature limit of V_f
V_W	upper bound on V
W	fractional mass of volatiles
w	proximate volatile matter
x_C, x_H	mass fractions of an element in the feed coal and spent char, respectively
Z	fractional loss of a particular element
Z_f	long-time asymptotic value of Z
Z_{fe}	high temperature limit of Z_f

Subscripts

- A based on uncorrected ash tracer method
- C feed coal
- H spent char

Superscripts

- + as received basis
- dry basis
- * dry ash-free (d.a.f.) basis

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